

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

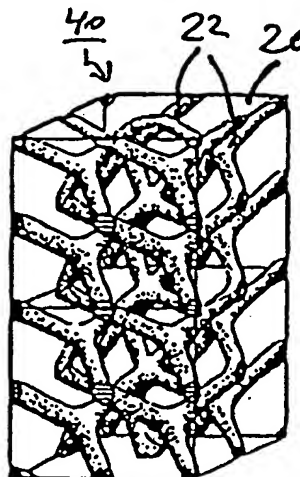
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : G02B 6/138	A1	(11) International Publication Number: WO 98/35248 (43) International Publication Date: 13 August 1998 (13.08.98)
(21) International Application Number: PCT/US98/02974 (22) International Filing Date: 11 February 1998 (11.02.98) (30) Priority Data: 60/037,902 11 February 1997 (11.02.97) US (71) Applicant (for all designated States except US): MASSACHUSETTS INSTITUTE OF TECHNOLOGY [US/US]; 77 Massachusetts Avenue, Cambridge, MA 02139 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): FINK, Yoel [US/US]; Apartment 14D, 60 Wadsworth Street, Cambridge, MA 02142 (US). THOMAS, Edwin, L. [US/US]; 14 Apple Ridge Drive, Natick, MA 01760 (US). (74) Agent: OYER, Timothy, J.; Wolf, Greenfield & Sacks, P.C., 600 Atlantic Avenue, Boston, MA 02210 (US).		(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: POLYMERIC PHOTONIC BAND GAP MATERIALS

(57) Abstract

A polymeric photonic band gap structure can be defined by a block copolymeric species, a mixture of homopolymers, or a combination optionally with appropriate dielectric contrast enhancing additives. The structure includes periodic, phase-separated microdomains alternating in refractive index, the domains sized to provide a photonic band gap in the UV-visible spectrum. Another method of the invention involves creating a defect in a polymeric article including a periodic structure of a plurality occurring separate domains. The defect can be created by inserting into the material a plane of a material different from materials defining the polymeric article. According to another method of the invention, a defect is created in a polymeric article, including a periodic structure of a plurality of periodically occurring separate domains, by altering polymeric material in the article. The polymeric material can be altered by removing polymeric material via radiation, by exposing the material to intersecting beams of radiation, by removing the material via etching or the like. A defect can be created in one embodiment by magnetically guiding a heated object through the article.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

POLYMERIC PHOTONIC BAND GAP MATERIALS

Field of the Invention

The present invention relates generally to polymeric materials that display periodic
5 ordering, and more particularly to a polymeric article defining an optical band gap material.

Background of the Invention

Photonic band gap materials, that is, materials that can control the propagation of
electromagnetic radiation by creating periodic dielectric structures, have been the subject of
vigorous research in recent years. A photonic band gap material is one that prohibits the
10 propagation of electromagnetic radiation within a specified frequency range (band) in certain
directions. That is, band gap materials prevent light from propagating in certain directions with
specified energies. This phenomenon can be thought of as the complete reflection of
electromagnetic radiation of a particular frequency directed at the material in at least one
direction because of the particular structural arrangement of separate domains of the material,
15 and refractive indices of those domains. The structural arrangement and refractive indices of
separate domains that make up these materials form photonic band gaps that inhibit the
propagation of light centered around a particular frequency. (Joannopoulos, et al., "Photonic
Crystals, Molding the Flow of Light", Princeton University Press, Princeton, New Jersey, 1995).
One-dimensional photonic band gap materials include structural and refractive periodicity in one
20 direction, two-dimensional photonic band gap materials include periodicity in two directions, and
three-dimensional photonic band gap materials include periodicity in three directions.

Ho, et al., "Existence of Photonic Gaps in Periodic Dielectric Structures", *Phys. Rev.
Lett.*, 65, 3152 (1990) correctly predicted that a properly-arranged, three-dimensional photonic
band gap material would include a complete band gap, that is, that the material would reflect
25 light of any polarization incident at any angle at a particular frequency. If one or more defects
are created in such a material, the material can serve a variety of useful purposes. Point defects
could define low loss optical resonance cavities, planar defects could define narrow-band filters,
and pathways within three-dimensional photonic band gap materials could define lossless
waveguides capable of guiding light around sharp corners, crucial to the creation of proposed
30 optical computers. Totally-reflective UV or laser shields, and countless other commercial
applications would benefit from relatively simple and reliable techniques for forming these
materials.

Fan, et al., ("Design of Three-Dimensional Photonic Crystals at Submicron Lengthscales", *Appl. Phys. Lett.*, 65, 11, 09/12/94) describe a class of periodic, three-dimensional dielectric photonic crystal structures amenable to submicron-scale fabrication. Fabrication involves creating a layered structure of materials alternating in dielectric constant, and etching (drilling) holes through the article normal to the layered structure. Specifically, the layered structure is created by depositing a layer of silicon on a substrate, etching grooves into the resulting silicon layer, and filling the grooves with silicon dioxide. Another layer of silicon is deposited on the first layer, grooves offset from those of the first set of grooves are etched, and those grooves filled with silicon dioxide. The process is repeated to create the multi-layered structure, through which the holes are etched. Assuming dielectric constants of 12.096 for silicon and 2.084 for silicon dioxide, (both at wavelength = 1.53 microns), the band gap was computed to extend from wavelength = 1.43 microns to 1.64 microns.

Joannopoulos, et al. (referenced above) provides an overview of photonic band gap materials, and their theoretical treatment. Experimental results are reported, including construction of a two-dimensional crystal lattice that reflects essentially all in-plane light within a specified frequency band. Specifically, construction involved etching a triangular lattice of air columns in a crystal via electron-beam lithography (see Wendt, et al., "Nanofabrication of Photonic Lattice Structures in GaAs/AlGaAs", *J. Vac. Sci. & Tech. B.* 11, 2637 (1993)). The columns of air were fabricated having a radius of 122.5 nm, the lattice constant was 295 nm, and the columns were about 600 nm tall.

Chen, et al., "Theoretical Prediction of the Optical Waveguiding Properties of Self-Assembled Block Copolymer Films", *Macromolecules*, 17, (1995) describe a lamellar-forming block copolymeric waveguide, and computer calculations of propagation constants and optical field intensity distributions of selected diblock and triblock copolymeric thin-film waveguides. It is reported that by choosing the chemical composition of each block, the refractive index of each layer can be precisely controlled. Where the refractive index of a guiding layer is greater than the refractive indices of the substrate and superstrate layers, a waveguide can result. Chen, et al. report that the domain size of individual lamellae can be varied from tens of angstroms to thousands of angstroms.

Three-dimensional periodicity in block-copolymeric, self-assembled structures are known. (Thomas, et al., "Phase Morphology in Block Copolymer Systems", *Phil. Trans. R. Soc. Lond. A.*, 348, 149-166). Lamellar, cylindrical, spherical, and ordered bicontinuous double

diamond morphologies in block copolymeric systems have been identified (see, for example, Helfand, et al., *Developments in Block Copolymers*. 1; Goodman, I., Ed.; Applied Science Publishers: London, 1982; vol. 1, pp. 99-126; Herman, et al., *Macromolecules*, 20, 2940-2942, (1987). Researchers have been successful in incorporation of metallic species, including
5 clusters, selectively in a first but not a second domain of a two-domain species resulting from thermodynamic phase separation of block copolymeric species Sankaran, et al., "Synthesis of Zinc Sulfide Clusters and Zinc Particles Within Microphase-Separated Domains of Organometallic Block Copolymers", *Chem. Mater.*, 5, 1133-1142 (1993); Sohn, et al., "Processable Optically Transparent Block Copolymer Films Containing Superparamagnetic Iron
10 Oxide Nanoclusters", *Chem. Mater.*, 9, 1, 264-269 (1997). Sankaran, et al. and Sohn, et al. pursued goals of creating monodisperse metal/semiconductor clusters in an organized array for the purpose of growing metal clusters in a controlled fashion for electrical, optical, magnetic, and catalytic applications. These and other techniques have shown some promise with respect to several diverse goals. However, there is a need in the art for inexpensive, simple, photonic band
15 gap materials, and it is an object of the present invention to provide such materials.

Summary of the Invention

The present invention provides a series of systems, polymeric materials, and methods associated with photonic band gap materials. The methods include methods of forming such materials and methods of use of such materials, and can be used in conjunction with any of the
20 systems or polymeric materials of the invention. That is, all of the systems described below can be made using the methods of making materials described, and can be used in the methods of using photonic band gap materials. The methods of manufacture and use of photonic band gap materials described herein can be applied to all of the systems or polymeric materials described herein.

25 In one aspect, the invention provides a series of systems. One system includes a polymeric article having a periodic structure of a plurality of periodically occurring separate domains. The domains include at least a first and a second domain that each have a characteristic dimension from about 50nm to about 1500nm. The article has a refractive index ratio of at least about 1.1 for a continuous set of wavelengths lying within a range from about 100nm to about 10
30 microns. That is, the article has a refractive index ratio of at least about 1.1 for at least one wavelength domain or continuous plurality of wavelengths, lying within a range of from about 100nm to about 10 microns.

In another embodiment, a similar system is provided. In this embodiment, the first and the second domains each have a characteristic dimension from about 15nm to about 50nm and a refractive index ratio of at least about 1.2 for a continuous set of wavelengths lying within a range from about 50nm to about 1000nm.

5 In another embodiment, a similar system is provided that has a characteristic dimension of from about 300nm to about 5000nm and a refractive index ratio of greater than 1.0. The refractive index ratio is for a continuous set of wavelengths lying within a range from about 400nm to about 50 microns.

10 In another embodiment, a system is provided that includes a structurally periodic polymeric structure including a defect in periodicity. The defect is at least partially transparent to electromagnetic radiation in a wavelength range of from about 100nm to about 50 microns. A portion surrounds the defect which is reflective to the electromagnetic radiation.

In another embodiment, a system is provided that comprises a polymeric article including a three-dimensional periodic variation in refractive index.

15 In another aspect, the invention provides a series of methods. One method involves exposing a portion of a polymeric article in an ordered state, having a pathlength to electromagnetic radiation within a free space wavelength range of from about 50nm to about 50 microns. The article is allowed to inhibit transmittance of the electromagnetic radiation to an extent greater than the article would inhibit that transmittance in a disordered state, at the
20 frequency through the pathlength.

Another method of the invention involves creating a defect in a polymeric article including a periodic structure of a plurality of periodically occurring separate domains. The defect can be created by inserting into the material a plane of a material different from materials defining the polymeric article.

25 According to another method of the invention, a defect is created in a polymeric article, including a periodic structure of a plurality of periodically occurring separate domains, by altering polymeric material in the article. The polymeric material can be altered by removing polymeric material via radiation, by exposing the material to intersecting beams of radiation, by removing the material via etching or the like. A defect can be created in one embodiment by
30 magnetically guiding a heated object through the article.

The systems or method of the invention can include at least one auxiliary refractive modifier in at least one of the first and the second domains. The refractive index modifier can be

particulate material, a dye, a polymeric particulate material, a ceramic, semi-conductor, or other particulate material, or the like, and can provide a refractive index ratio in the article of greater than 1, or at least about 1.1, 1.2, 1.3, 1.4, 1.5, 2.0, or 4.0, in other embodiments.

The systems and methods of the invention can involve a polymeric article that has a one-dimensional structure, a two-dimensional periodic structure, or a three-dimensional periodic structure, and can be formed from polymeric materials that are self-assembled from self-assembly of polymeric materials to form separate domains followed by removal of one domain and replacement with a additive material such as a non-polymeric material. That is, first and second domains can be formed by polymeric self-assembly of the first domain and a polymeric precursor of the second domain, followed by replacement of the precursor by a non-polymeric material.

The systems and methods of the invention can involve a polymeric article that includes a block co-polymer having at least two Blocks A and B that are assembled into the first and second domains, respectively. The polymeric article can also include at least three blocks, A, B and C wherein the blocks A and B are self-assembled into the first and the second domains.

The systems and methods of the invention can include polymeric articles that include at least one defect in periodicity. The defect in periodicity can be a point, line, planer defect, or combination thereof, and the defect can have a width, length and height. Where the polymeric article is at least two-dimensionally periodic, the defect can be provided in at least one of the two dimensions, or in two dimensions. Where the polymeric article is three-dimensionally periodic, the defect can be provided in one, two or three dimensions. The defect can be a series of interconnected points, or a line having a width and a length at least five times the width, and other geometric arrangements. A defect can be a continous pathway that is non-linear, and can be three-dimensionally non-linear. The defect can be in the order of diolectric domains of the structure and can be a defect in refractive index between at least two adjacent domains of a polymeric article.

In some embodiments, the polymeric article of systems or methods of the invention can include a metallic species, rather than a refractive index-modifying species. The metallic species can be a refractive index-modifying species, or another metallic species residing primarily in one domain, selectively.

Systems or methods of the invention can include polymeric articles that are periodic arranged structures of a plurality of separate domains. The structure can inhibit transmittance of

electromagnetic radiation at a free-space wavelength range from about 50nm to about 50 microns relative to transmission of electromagnetic radiation at the wavelength through a system comprised of the same materials, but in a disarranged state. These structures can inhibit transmittance at a free-space wavelength range of from about 300nm to about 50 microns in other emodiments. A periodic arranged structure can be provided in accordance with systems or methods of the invention that has a photonic band gap in at least one direction within a free-space wavelength range of from about 50nm to about 50 microns. A periodic arranged structure can have a photonic band gap in at least one direction within a free-space wavelength range of from about 300nm to about 50 microns.

Systems or methods of the invention can include polymeric articles that in a disarranged state, are at least partially transparent to light within a wavelength range of from about 100nm to about 10 microns, or a wavelength range of from about 400nm to about 50 microns.

The invention also provides systems that are block copolymers. One block copolymeric species has at least two blocks A and B. The blocks A and B are incompatible with each other such that the block copolymer species is self-assembleable into a periodic structure of a plurality of at least first and second, separate domains, each defined by association of similar blocks of the copolymer species. The periodic structure into which the block copolymer species is self-assembleable is able to contain at least one auxiliary index of refraction enhancing additives such that the first and second domains have a refractive index ratio of at least 1.1 at a wavelength of from about 100nm to about 10 microns, or other refractive index ratios for a continuous set of wavelengths lying within ranges as described herein. In one embodiment, the molecular weight of the block copolymeric species is at least 80,000 Daltons. In another embodiment, the molecular weight is at least 500,000 Daltons, and in another embodiment, at least 2,000,000 Daltons.

Another method of the invention involves a method for processing a block co-polymer. In one embodiment, a block copolymer is processed to produce a phase-separated polymeric multi-domain structure. The structure includes a periodic variation in refractive index of a dimension on the order of from about 100nm to about 50 microns, to the extent that the article defines a photonic band gap structure. The block co-polymer can be allowed to self-assemble into the phase-separated polymeric multi-domain structure and this can occur in the presence of an applied, electric, magnetic, or mechanical flow field in certain embodiments. In one preferred embodiment, the phase-separated structure is self-assembled in the presence of an applied

electromagnetic field.

Systems of the invention can include a metallic coating on metallic particles that reside primarily in one domain selectively.

Other advantages, novel features, and objects of the invention will become apparent from
5 the following detailed description of the invention when considered in conjunction with the accompanying drawings, which are schematic and which are not intended to be drawn to scale. In the figures, identical or nearly identical component that is illustrated in various figures, is represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is
10 not necessary to allow those of ordinary skill in the art to understand the invention.

Brief Description of the Drawings

Fig. 1 is a schematic illustration of a polymeric one-dimensional photonic band gap material;

Fig. 2 is a schematic illustration of a polymeric one-dimensional photonic band gap
15 material including auxilliary refractive index modifying and periodicity enlarging species;

Fig. 3 is a schematic illustration of a polymeric two-dimensional photonic band gap material;

Fig. 4 is a schematic illustration of a polymeric three-dimensional photonic band gap material; and

20 Fig. 5 is a schematic illustration of another three-dimensional photonic band gap material.

Fig. 6 is a Transmission electron microscope micrograph of a layered photonic band gap polymer system showing the formation of periodic dielectric domains;

Fig. 7 is a Small Angle X-ray trace a layered periodic high dielectric contrast photonic band gap polymer system;

25 Fig. 8 is a Transmission electron microscope micrograph of a two-dimensional photonic band gap polymer system comprising cylinders on a triangular lattice showing the formation of periodic dielectric domains;

Fig. 9 is a Small Angle X-Ray trace of a layered periodic high dielectric contrast two-dimensional photonic band gap polymer system;

30 Fig. 10 is a Small Angle X-Ray trace of a layered periodic high dielectric contrast two-dimensional photonic band gap polymer system with global order enhanced by annealing;

Fig. 11 is a calculated dispersion relation for low dielectric-constant cylinders in a high

dielectric matrix showing an omnidirectional photonic band gap.

Detailed Description of the Invention

The invention provides a polymeric system arranged as a photonic band gap material that inhibits the propagation of a selected frequency of electromagnetic radiation in at least one direction. The term "polymeric system" or "polymeric article" as used herein includes any system or article constructed at least in part from at least one polymer material. The polymeric systems of the invention are inexpensive, allow large area coverage, are mechanically flexible, and, in certain embodiments, self-assemble. The invention provides one, two, and three-dimensional polymeric articles having periodic dielectric structures resulting in polymeric band gap articles that exhibit a band gap inside a specified frequency range in one dimension, two dimensions, or three dimensions. That is, the polymeric articles of the invention inhibit the propagation of electromagnetic radiation at wavelengths in the material ($\lambda_{\text{free space}}/n_{\text{effective}}$) on the order of the periodicity length of the material in at least one direction, two directions, and a plurality of directions including omnidirectional. With the addition of one or more defects, the arrangement can be used to cause light to propagate along planes, along lines, through non-linear and non-planar continuous pathways, through spaces, and into points. The periodicity of the polymeric systems of the invention and the size of the domains within the systems can be altered, for example by deforming the polymer. For example, periodicity can be altered by mechanical means, such as drilling holes in a system or cutting a system along a specific plane, thermal means, such as selective melting of portions of a system with hot probes or lasers, chemical means, such as selective etching or chemical modification of portions of a system, through selective manipulation of processing procedures, such as processing under the influence of an external field, roll casting, or additions of impurities into one or portions comprising a system, and via a variety of other means hereinafter described or apparent to one of ordinary skill in the art. The dielectric contrast, as well as the periodicity of the periodic dielectric structure, can be varied. In some embodiments, the structure need not be strictly periodic but may be modulated by a field gradient or other modulating means.

The band gap articles of the invention are not limited to use with visible light, although articles operating in the visible light spectrum are preferred. The photonic band gap articles of the invention that operate in the visible light range can be used for low loss waveguides capable of guiding light through non-linear, non-planar pathways that can include sharp corners, or angles of essentially any degree of acuteness. The articles can be used in connection with optical

computers, frequency and angle of incidence dependent highly reflective coatings, microcavities useful as optical resonators, totally-reflective visors, etc. The invention avoids problems inherent in connection with most current photonic band gap articles. Most current research efforts concentrate on semiconducting materials such as Si, GaAs, or InP, and are aimed at the
5 construction of two and three-dimensional band gap structures using a variety of lithographic and etching techniques. Problems associated with these approaches include the limited ability of forming intricate, three-dimensional structures on the scales necessary for use as effective band gaps.

The present invention makes use of polymeric materials. The materials can include, but
10 are not limited to, homopolymers, blends of homopolymer, copolymers including random and block copolymers, blends of copolymers, blends of homopolymers and copolymers, and any such systems combined with additives such as dyes, particles, heavy atoms, metallic coating materials, and the like. The systems of the present invention comprise polymeric materials, or mixtures of polymeric materials, or mixtures of polymeric materials and other, non-polymeric materials, and
15 include two or more distinct domains of different composition and/or physical, chemical, or optical properties.

The term "domain", as used herein, defines a distinct region of the system characterized by a particular effective dielectric constant or particular effective refractive index that differs from that of surrounding or adjacent domains. Domains are not necessarily defined by a
20 particular material. These distinct domains are comprised of species, including one or more polymeric species for at least one domain. Where a domain is defined by a polymeric species it is referred to as a "polymeric block." That is, the domains, where polymeric, are based on distinct polymeric blocks that can be comprised of a variety of components comprising distinct regions of the structure, and in each embodiment of the invention at least one domain is
25 polymeric. The polymeric blocks typically are formed from phase-segregated, polymeric species that are immiscible with polymeric species of adjacent phases (which can define domains) from which they are segregated where the species comprising each separate phase defines separate polymeric blocks corresponding to each phase. That is, adjacent polymeric blocks that can define adjacent, distinct domains can be defined by immiscible mixtures of homopolymer species or
30 random copolymer species, or chain regions (blocks) of a block copolymer that are comprised of a immiscible monomer sequences, or mixtures of the above with or without other non-polymeric additives, where the species in each separated phase or region formed define a polymeric block.

Systems comprising multiple polymeric blocks can be comprised of one or more block copolymers or polymeric mixtures involving various blends of homopolymers and/or random copolymers with block copolymers, for example: a homopolymer or random copolymer comprising a block A with a block copolymer comprising blocks A'+B, where A and A' are miscible and are incompatible with B such that the homopolymer or random copolymer A forms a polymeric block in combination with block A' of the block copolymer and block B' of the block copolymer forms a distinct polymeric block; or a homopolymer or random copolymer comprising a block A, a block copolymer comprising polymeric blocks A'+B, and another homopolymer or random copolymer defining a block B', where A and A' together are miscible and form a polymeric block and B and B' are together are miscible and form a polymeric block. It is to be understood that the preceding examples are only exemplary, and that those skilled in the art would readily conceive of additional examples which are within the scope and spirit of the invention. In one preferred embodiment, the present invention makes use of self-assembling polymeric systems, for example block-copolymeric systems and blends of various polymers that can include block-copolymers to form one, two, and three-dimensional structures that can, in certain embodiments, be topologically connected. As used herein, "topologically connected" means continuous, in the sense that a particular domain in a periodic, polymeric structure forms a continuous pathway through the structure. This term is defined to include physical connection, or at least proximity to the extent that a photonic band gap material results.

The refractive indices of separate domains of the structures, and periodicity in structural arrangement, are tailored to meet desired criteria. The periodicity in structural arrangement is met by creating separate domains of size similar to the wavelength (in the material comprising the domain as opposed to in a vacuum (freespace)) of electromagnetic radiation desirably blocked by the band gap structure, preferably domains of size no greater than the wavelength of interest. The wavelength of electromagnetic radiation in a material can be related to the wavelength of the radiation in freespace by the following relationship: $\lambda_{\text{material}} = \lambda_{\text{freespace}}/n_{\text{material}}$ where n_{material} is the effective index of refraction of the material at that wavelength. The refractive index ratios between adjacent domains should be high enough to establish a band gap in the material. Band gap can be discussed with reference to two related ratios, the dielectric constant ratio ($\epsilon_1/\epsilon_2 = n_1^2/n_2^2$) and refractive index ratio (n_1/n_2), where n_1 is the effective index of refraction of a first domain and n_2 is the effective index of refraction of a second domain. In general, the larger the refractive index ratio (refractive contrast) the larger the band gap and, in

the present invention, band gap is tailored to be above a predetermined threshold and extends in one dimension for one-dimensional systems, two dimensions for two-dimensional systems, and three dimensions for three-dimensional systems. Preferably, adjacent, dissimilar domains differ in refractive index such that the ratio of the refractive index of one to the other is at least about 1.1 for a continuous set of wavelengths lying within a wavelength range of from about 100nm to about 10 μ m, or, for some embodiments, more preferably at least about 1.2, 1.3, 1.4, 1.5, 2, 4, or 7 within a wavelength range of from about 100nm to about 10 μ m. According to another set of embodiments, these preferred refractive index ratios exist for a continuous set of wavelengths lying within a wavelength range of from about 300 to about 700 nm, and according to another set of embodiments, the ratio of refractive index of one to the other is at least 1.0 for a continuous set of wavelengths lying within a wavelength range of from about 400 nm to 50 μ m, and according to yet another set of embodiments, the ratio of refractive index of one to the other is at least 1.2 for a continuous set of wavelengths lying within a wavelength range of from about 50 nm to 1000 nm. These dielectric structures, exhibiting a band gap in their dispersion relation, cannot support electromagnetic waves at certain frequencies thus those waves are inhibited from propagating through the material.

The polymeric structure should be made of material that, in a disarranged state (not arranged with the periodic structure necessary for photonic band gap properties) is at least partially transparent to the electromagnetic radiation of interest. When the material is at least partially transparent to the electromagnetic radiation of interest, defects in the ordered domain structure of the photonic band gap material define pathways through which the electromagnetic radiation can pass since the criteria for blocking the radiation is destroyed.

Figs. 1-5 are schematic illustrations that are representative of self-assembled, periodic polymeric structures arranged as photonic band gap articles. The propagation of electromagnetic radiation in the articles of the invention represented by Figs. 1-5 is governed by Maxwell equations, and reference can be made to Joannopoulos (above) for a detailed treatment of the physics involved. In the following discussion of length scales and periodicity, for the sake of simplicity, reference will be made primarily to band gap structures comprised of two separate domains (A and B) with simple one dimensional periodicity. It is to be understood, however, that the invention encompasses systems with greater than two separate domains, and with two- or three- dimensional periodicity. In such systems, as would be understood by those of ordinary skill in the art, the determination of effective domain and periodicity length scales becomes more

complex and is affected by factors such as geometric configuration, relative refractive contrast, and others. Incorporated herein by reference Joannopolous, et al. "Photonic Crystals, Molding the Flow of Light", Princeton university press, Princeton, New Jersey, 1995 describes such systems.

5 Referring now to Fig. 1, a one-dimensionally periodic polymeric photonic band gap article 10 is illustrated schematically. Article 10 is made of a series of essentially planar layers 12, 14, 16, and 18 stacked in the X-Y plane, layers 12 and 16 comprising domains and being defined by a first polymeric species 20 and layers 14 and 18 being defined by a second polymeric species 22. At least one of these polymeric species can also include one or more auxiliary
10 components such as domain dimension modifiers, processing aids, and/or refractive index-modifying species. Polymeric species 20 and 22, including any additive species, preferably differ in refractive index such that the refractive index ratio of the two polymeric species, including any additive species, is as defined above. Thus, article 10 includes a periodic structure of alternating first domains 12 and 16 and second domains 14 and 18 that are dissimilar, and
15 differ in refractive index. Each of layers 12 and 16 has a domain characteristic dimension l_A and each of layers 14 and 18 has a domain characteristic dimension l_B , where the domain characteristic dimensions are proportional to the end to end root mean square (RMS) length of the polymeric species, or copolymer block, comprising each layer in the phase separated state, such that the periodicity, or periodic length, L of the periodic dielectric structure can be
20 represented, for this simple one-dimensional case, as $L = l_A + l_B$, and is on the order of the wavelength (in the material) of electromagnetic radiation 26 desirably blocked by the article. For more complicated configurations, the periodic length L is proportional, but not necessarily equal to the sum of the characteristic domain dimensions. When these criteria are met, exposure of the article, in a direction normal to the planes of the layers 12-18 in the Z axis, to electromagnetic
25 radiation of a wavelength on the order of L , results in total reflection of the radiation. Fig. 2 shows an embodiment of a one-dimensional structure having polymeric blocks 20 and 22 which include blocks A and blocks B, respectively, of a diblock copolymer. Polymeric block 22 of the embodiment shown in Fig. 2 is comprised of a mixture of block B of the copolymer, particles 23, and a homopolymer C 24.

30 If polymeric species 20 and 22 are at least partially transparent to electromagnetic radiation 26 to which the article is exposed, and if a defect in periodicity exists in the article that disrupts the ordered, structured arrangement of the article in at least a portion, then the radiation

can propagate into and/or through that defect. In one-dimensional periodic systems, a defect can be a change in the index of refraction or the thickness (l) of one layer. An observer located within a defect and looking in the direction of the periodicity will see highly reflective walls, the defect thus being useful in selective propagation of light in photonic band gap materials. A defect can be a continuous pathway, that is, a pathway having a width and a length at least ten times its width. The defect can be a void (i.e., air or other material surrounding the article), one of the polymer species 20 or 22, or any other medium at least partially transparent to the electromagnetic radiation blocked by the defect-free arrangement. Electromagnetic radiation striking the article at regions other than the defect does not propagate through the article, but radiation striking the defect passes through the article to the extent that the defect exists. The radiation of interest, in the defect, can only propagate within the defect due to essentially complete destructive interference in the article beyond the boundary of the defect. Point-like defects (hereinafter referred to as point defects), that is, defects that are small isolated regions, can be created as well, thus forming single, or multi mode cavities.

In a photonic band gap system, such as the one-dimensional photonic band gap material illustrated in Fig. 1, the separate domains 12, 14, 16, and 18 need not alternate in refractive index, but the article can be made up of polymeric species, including any additive species, in sections 12, 14, 16, and 18 that incrementally increase or decrease in refractive index. For example, section 12 can have a refractive index of 1.1, section 14 a refractive index of 1.2, section 16 a refractive index of 1.3, etc., and the article will include a refractive contrast between domains that can be useful.

Referring now to Fig. 3, one possible configuration of a two-dimensionally periodic polymeric photonic band gap article 28 is illustrated. Article 28 includes periodicity in both the X direction and Z direction, but not in the Y direction. The article is made up of a plurality of pillars, or columns, arranged axially in the Y axis, article 28 is defined by a plurality of cylindrical polymeric domains of polymeric species 22 extending in the Y axis of the structure, separated by polymeric species 20. The article is a two-dimensional band gap structure and will reflect radiation of wavelength (in the material) on the order of the characteristic domain dimension of polymeric domain 22 in cross-section (X-Y plane), or the periodic length, which is proportional to the distance between adjacent columns. This radiation will be essentially reflected if directed at the article anywhere in the X-Z plane. The article will pass this radiation in the Y direction. A defect passing through the article in any direction in the X-Y plane,

including a defect pathway including sharp corners, will propagate light and serve as a light guide. One way of creating a defect is to remove a series of columns of polymeric species 22 in a pathway.

Referring to Fig. 4, a three-dimensionally periodic polymeric photonic band gap article 32 is illustrated which is periodic in terms of polymeric species 20 and 22 in each of the X, Y, and Z directions at a periodic length L. The structure of Fig. 4 is a double gyroid arrangement of polymeric species 22 surrounded by polymeric species 20. Because periodicity in dielectric constant exists in every dimension, article 32 may be reflective to electromagnetic radiation of a wavelength on the order of L in all directions. A defect, which can be three-dimensionally non-linear (can change in direction of displacement in any direction), will pass electromagnetic radiation of wavelength on the order of L even if the defect includes sharp corners including very acute angles. Since radiation can exist anywhere within the defects and is evanescent beyond the defect boundary, light path bending at any angle including a complete reversal in direction of propagation is possible.

Fig. 5 illustrates a polymeric, three-dimensional photonic band gap article 40 including an arrangement of polymeric species 22, in double diamond configuration, surrounded by polymeric species 20.

Polymeric species 20 and 22 can be arranged periodically, as illustrated in Figs. 1-5, in a variety of ways. According to one technique, polymeric species 20 and 22 define different blocks of a block copolymer. The block copolymer includes blocks of species 20 alternating with blocks of species 22, the copolymer self-assembles into a periodically ordered, structured array. Either of the species (association of blocks) 20 and 22 can also include one or more compatible auxiliary (additive) species. Auxiliary species may be desirable to control characteristic domain dimensions, refractive indices, or both. In other embodiments, a copolymer can be used that includes more than two phase separable blocks, for example a triblock copolymer.

The polymeric species used for both domains 20 and 22, are preferably below their melt temperature and preferably below their glass transition temperature at service temperatures (i.e., within a temperature range of at least from about -100°C to about 250°C. For embodiments involving self-assembled polymeric articles, the articles are formed by a mixture of polymeric species, or block copolymer chains each including at least one first polymeric block of species 20 and at least one second polymeric block of species 22 immiscible with the first block. The

polymeric species are selected such that, at a temperature above melt temperature or in solution in a suitable solvent, they are segmentally mixed and upon, for example, solidification from a melt or evaporation of a solvent from a solution, the ordered structure is formed including a continuous matrix of amorphous domains. For embodiments involving block copolymers, the amorphous
5 domains are typically defined by association of the first blocks and second blocks of the copolymer, respectively. In some embodiments, a liquid crystalline domain is incorporated that has anisotropic optical properties (indicatrix; second rank refractive index tensor).

For embodiments where the systems are self-assembled, components for forming a polymeric mixture or block copolymer defining species 20 and 22 as exemplified can be selected
10 according to the following criteria: The polymeric mixture or block copolymer forms separate domains upon phase separation occurring from solidification (including via evaporation from a solvent); one or both components can be below T_g or T_m . Species used in the polymeric mixture or defining the block copolymer form the ordered structure in a manner such that global dimensional stability of the structure exists. As used herein, "microphase separation" means a process in which
15 polymeric blocks are locally segregated to form ordered domains.

That is, a polymeric mixture or block copolymer that defines both species 20 and 22, according to embodiments involving self-assembled articles, is an association of polymer or block copolymer chains in which inter-chain/block, non-covalent chemical attraction such as polar/polar or polar/induced polar interactions, including hydrogen bonding, or nonpolar/nonpolar interactions
20 including Van der Waals interactions, create association between the chains that promotes domain formation while maintaining a degree of dimensional stability required for a particular application. This non-covalent, chemical attraction of species comprising polymeric blocks to each other results in unique thermodynamic and rheological behavior. At high temperatures, or in solution, the polymeric mixtures or block copolymers form isotropic phases in which the different species
25 comprising the different polymeric blocks are randomly or, in the case of block copolymers, segmentally mixed. Upon lowering the temperature or evaporating away the solvent, or upon precipitation from solution, the repulsion between unlike species or segments increases, causing the polymeric mixture or copolymer to phase separate locally into distinct regions (For the case of block copolymers, each region is composed of one of the block components). These segregated regions
30 subsequently organize into ordered periodic structures, the morphology of which is governed by,

among other things, the relative volume fractions of the different polymeric blocks, which can depend on the molecular weight of the species comprising the polymeric blocks and presence of additives. Global dimensional stability is imparted to the material.

The following discussion on miscibility will aid those of ordinary skill in the art in selecting
5 suitable first and second blocks for a copolymer that defines species 20 and 22, or for separate polymers that define these species, or a combination (i.e. a block copolymer that includes one or more auxiliary polymeric species associated with one or more domains). This discussion can be generalized also to a higher order block copolymer, such as a triblock (A-B-C) copolymer. For an example of a diblock copolymer of N total segments, with a 50:50 volume composition, $\chi N > 10.5$
10 for block segregation. The critical value of χN is larger if the volume composition is different from 50:50. For asymmetric A-B diblock copolymer compositions, the value of χ required for block segregation can be calculated from a well-known formula by L. Leibler (Macromolecules 13, 1602 (1980)), while for A-B-A triblock copolymers, a similar formula by A. M. Mayes and M. Olvera de la Cruz (J. Chem. Phys. 91, 7228 (1989)) can be employed to calculate values of χ required for
15 phase separation for any composition and molecular weight. Those of ordinary skill in the art can carry out this determination technique, and can determine the critical composition for a given diblock or triblock copolymer of any N and composition and can also use similar criteria, readily available, for other types of phase-separable polymeric mixtures.

The molecular weight of polymer or copolymer components defining species 20 and 22
20 should be selected to be high enough so that a segregated morphology in the service temperature range of the photonic band gap material is maintained. Specifically, the molecular weight typically is at least about 10,000, preferably at least about 15,000, more preferably at least about 25,000. In one set of embodiments the periodic length L, proportional to the sum of the characteristic domain dimensions l_A and l_B is related to the molecular weight of the species comprising each domain. In
25 this set of embodiments, the molecular weight of polymer or copolymer components defining species 20 and 22 should be at least about 50,000 Daltons, more preferably at least about 100,000, more preferably still at least about 300,000, more preferably still at least about 600,000, and more preferably still at least about 2,000,000 Daltons.

A non-limiting list of polymeric or block copolymeric species can include those that are
30 defined by or contain blocks of polystyrene, polybutadiene, polyisoprene, polycaprolactone,

polyethyleneoxide, poly 2-vinyl pyridene, polydimethyl siloxane, and the like. A vast array of different block copolymers, combinations of different homopolymeric species, or combinations of block copolymeric and homopolymeric species can be used in accordance with the invention so long as other criteria described herein are met. Polymers and block copolymers can include a wide
5 variety of side chains that exist naturally, and/or that exist to alter refractive index, segregated polymer domain size, or a combination. For embodiments where structures are self-assembled, each of the first and second polymeric blocks can be a mixture of components so long as the polymer phases separate into the ordered structure described.

Synthetic procedures such as anionic synthesis, Ziegler-Natta polymerization and ring-
10 opening metathesis polymerization (ROMP) (see, for example, Odian, G. "Principles of Polymerization" 2d Ed., Wiley, New York; "Principles and Applications of Organotransition Metal Chemistry", Collman, J.P., Hegedus, L.S., Norton, J.R., and Finke, R.G., University Science Books, Mill Valley, California, 1987, p 590; Grubbs, R.H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F.G.A.; Abel, E.W., Eds.; Pergamon: New York, 1982; Vol. 8, Chapter 54, p
15 502; Dragutan, V.; Balaban, A.T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerization of Cycloolefins*; Wiley, New York, 1986; Dolgoplosk, B.A.; Korshak, Yu.V. *Russian Chem. Rev.*, 1984, 53, 36) are well-suited for the preparation of a block copolymeric species defining species 20 and 22 with well-defined molecular weights and compositions. Alternatively, block copolymers can be prepared by the reaction of end-functionalized homopolymers, by addition polymerization of one
20 block component onto an end-functionalized homopolymer, or by sequential addition of two monomer species in a living free radical polymerization. In some embodiments, a photonic band gap article can be prepared by processing, such as melt pressing, or solvent casting techniques such as spin coating or slow evaporation. Technologies for synthesizing and processing such polymeric species are well-known to those of ordinary skill in the art, and includes roll casting or shear casting
25 to achieve near single crystal texture (see, for example, Albalak, R. J., Thomas, E. L., "Microphase Separation of Block Copolymer Solutions in a Flow Field", *J. Polym. Sci., Polym. Phys. Ed.*, p 37-46).

Adjustment of the refractive indices of polymeric species comprising domains 20 and 22 can be made by using, or synthesizing, a polymeric mixture or a block copolymer that includes species
30 20 and 22 of differing refractive indices; provision of a polymeric mixture or a block copolymer

with different species 20 and 22 that phase separate but that do not necessarily include a requisite difference in refractive index and addition of a refractive index-adjusting additives such as an auxiliary polymer that is compatible with one of the phases only (to adjust that phase in refractive index relative to the other phase); provision of a polymeric mixture or a block copolymer with
5 different species 20 and 22 and chemical modification of one or both of the species 20 or 22 to change dielectric constant of one or both; or the like.

Most polymeric species have a refractive index ratio of from between about 1.4 to about 1.7. Accordingly, in some instances a particular combination of polymeric species, or combination of blocks of a block copolymeric species may not have a refractive index contrast needed for
10 establishment of a suitable band gap. For example, polystyrene and polybutadiene have a small difference in refractive index. Therefore, in a polystyrene/polybutadiene mixture or block copolymer it may be desirable to alter the refractive index of one or both of the species.

One technique for selectively altering the refractive index of one domain of a multi-domain polymeric article is to create a polymeric article including a periodic structure of a plurality of
15 alternating separate domains, and changing the refractive index of one domain. Where a block copolymeric species is involved, this will involve changing the refractive index of one of the blocks that has phase-separated into a separate domain. One technique for changing the refractive index of a domain can involve creating a polymeric domain that includes a metal atom on a side group, and forming clusters within that polymeric domain. Formation of clusters containing metal atoms on a
20 polymeric chain can be carried out by forming a microphase-separated structure and diffusing a reactant selectively into the polymeric domain in which it is desired to create clusters. Such a technique is described by Sankaran, et al., "Synthesis of Zinc Sulfide Clusters and Zinc Particles Within Microphase-Separated Domains of Organometallic Block Copolymers", *Chem. Mater.*, 5, 1133 (1993), incorporated herein by reference. In the technique described by Sankaran, et al., block
25 copolymers of methyltetracyclododecene (MTD) and 2,3-trans-bis((tert-butylamido)methyl)norborn-5-ene(ZnPh)₂ [bTAN](ZnPh)₂ were prepared via ROMP to create block copolymers exhibiting either lamellar or spherical microphase-separated morphology. The zinc atoms in the organometallic domains of the block copolymers were converted to either metallic clusters of zinc or semi-conductor clusters of zinc sulfide by appropriate thermal or chemical treatment. Thermal treatment
30 can involve heating in a bomb reactor and chemical treatment makes use of the fact that the

organometallic phase of the microphase-separated structure is compatible with water, and involves treatment of the polymeric species with aqueous H_2S to create ZnS in that domain. Another technique that can be used in the present invention is one similar to that described by Sohn, et al., "Processable Optically Transparent Block Copolymer Films Containing Superparamagnetic Iron Oxide Nanoclusters", *Chem. Mater.*, 9, 264-269 (1997), incorporated herein by reference. Iron oxide nanoclusters are formed, selectively, within one domain of a multi-domain phase-separated polymeric article. In the technique described, the block copolymer $[NORCOOH]_{30}[MTD]_{300}$ (NORCOOH = 2-norbornene-5,6-dicarboxylic acid; MTD = methyltetracyclododecene) is synthesized using an alkylidene initiator $(Mo(ChCMe_3Ph)(NAr)(O-t-Bu)_2$ (Ar=2,6-diisopropylphenyl). The microphase-separated polymeric structure includes topologically-connected carboxylic acid-containing domains that provide a selective diffusion path for aqueous reagents. Accordingly, aqueous NaOH treatment of the assembled structure results in oxidation of iron hydroxide units to iron oxide units in the presence of ambient oxygen. Agitation of the polymeric structure can assist oxidation and flushing and agitation can be used to remove NaOH and NaCl residues. Oxide nanoclusters are formed predominantly within the interconnected domains that originally are NORCOOH. The present invention makes use of this technique for adjusting the refractive index of a polymeric domain, selectively.

In another, similar, technique, a polymeric mixture or block copolymer, does not include species with a metal atom-containing group or a moiety that is reactive with the metal atom-containing group, but includes a polymeric block that is selectively compatible with a homopolymeric species that does include a metal atom-containing group or a moiety reactive with a metal atom-containing group. Admixture of the polymeric mixture or block copolymer and the homopolymeric species results in a phase-separated structure including one set of domains carrying, selectively, the homopolymeric species. Reaction of the homopolymeric species to form nanoclusters of metal, metal oxide, metal sulfide, ceramics, semiconductors, or the like is carried out as described above to create clusters that reside, selectively or predominantly, in one domain, creating the requisite refractive index ratio. It is not requisite that nanoclusters, or clusters of any type be created according to this refractive index-adjustment technique, only that a particular domain be amenable to receiving, selectively or predominantly relative to others, a refractive index-adjusting species.

Zimmermann, et al., "High Refractive Index Films of Polymer Nanocomposites", *J. Mater. Res.*, 8, 7, 1742 (1993) describe increasing the refractive index of gelatin from 1.5 to 2.5 by creating colloidal PbS within the gelatin via agitation of a gelatin/lead acetate solution while adding hydrogen sulfide. This technique can be applicable to refractive index adjustment of domains of
5 polymeric articles of the present invention.

In another technique, polymeric species including nanoclusters or colloidal particles of refractive index-adjusting species can be created, and later assembled into microphase-separated polymeric domains.

Another technique for adjusting the refractive index of one domain of a multi-domain
10 polymeric article selectively is to form additives such as latex particles, and add these particles to a mixture of polymeric species (including, by definition, different blocks of a block copolymeric species) in which one of the species is compatible with the particles to an extent greater than the other polymeric species (or other block or blocks of a copolymeric species). The additive can be any refractive index-adjusting species such as metal or metal-containing nanoclusters, as described
15 above. The compatibility of the additive for one polymeric species (or block) selectively is great enough that, when a periodic structure of alternating first and second separate domains defined by the different polymeric species is created, the additive will segregate predominantly or selectively in one species to create the requisite refractive index contrast. The additive can be added to the species prior to formation of the periodic structure or, where the additive takes the form of small enough
20 particles, it can be diffused selectively into one or more domains in a carrier that is selectively compatible with those domains. Alternatively, it can be diffused into all domains via one or more carriers, and subsequently removed from one or more domains selectively via a flushing carrier that is compatible selectively with the domains from which the species is removed, or via a flushing carrier that is compatible with all domains where the additive is selectively incompatible with
25 domains from which it is to be removed. In this arrangement, the additive particulate species may form a high volume percent of one type of domain in a microphase-separated structure. That is, one domain may include the particulate species at a high level, even greater than 50% by volume, and the polymeric species in that domain can define essentially a surfactant that holds the particulate species in place, and together with the particle size, determine the periodicity. This type of
30 arrangement, in which a high-level of additive is held predominantly in one domain by a polymeric

species that acts essentially as an additive, falls within the definition of a separate domain in a periodic polymeric photonic band gap structure.

In another technique for adjusting refractive index, a multi-domain structure is formed, defined by different polymeric species or different blocks of a copolymeric species, or both, a monomeric or cross-linkable species is added to the structure that migrates selectively to one domain, and that monomeric or cross-linkable species is polymerized or cross-linked in situ to form a portion of that domain. Species can be graft-polymerized onto existing polymeric species in this manner. In this technique separate monomeric or cross-linkable species can be introduced into separate domains and polymerized, cross-linked, or grafted simultaneously or sequentially to change the refractive index of more than one domain.

In another technique for adjusting refractive index of a domain, selectively, a periodic, polymeric, microphase-separated structure can be fabricated such that one domain is etchable and another is not. That is, the structure is fabricated such that exposure of the structure to an etchant will result in dissolution and removal of one phase selectively while another phase remains intact.

With reference to Fig. 3, this could involve exposing article 28 to a chemical reactant that selectively removes species 22, leaving species 20 intact. This can be accomplished when species 20 is chemically inert with respect to the etchant, or is converted to a resistant material (for example, a Si-containing block can be converted to SiO_2) and is robust enough to maintain structural integrity upon removal of species 22. Creating a species 20 that is robust enough to withstand the etchant can involve creating physical rigidity in species 20 via, for example, crystallinity, cross-linking, additive of a dopant selectively to species 20 that causes cross-linking, and the like. After species 22 is selectively removed, it can remain as is (defining a periodic void structure filled by surrounding fluid such as air or another fluid that includes a desired refractive index) or a second species can be added to the resultant voids and retained in situ via solidification. Solidification can involve precipitation, cross-linking, or the like.

Another technique for adjusting the refractive contrast between different polymeric phases 20 and 22 is by selective staining of one of the periodic phases with a dye.

Characteristic dimensions of the individual domains that make up the periodic band gap structure can be controlled by adjusting the length of one or more polymeric species (or blocks of a phase-separated block copolymer) that defines the structure, adjusting polymer processing

conditions that increase or decrease the stacking, coiling, or other arrangement of polymer chains (or copolymer blocks), addition of homopolymers, etc. Ring-opening metathesis polymerization, reference above, or anionic synthesis (Cohen, et al.; referenced above), are techniques that can find use in the invention for creating polymer domains of desired size since they well-defined synthetic
5 technique that avoids side reactions and that allows control over molecular weight of particular blocks of block copolymers, or molecular weights of polymeric species. High-molecular-weight multi-block copolymeric systems can be synthesized according to the technique by initiating a polymerization reaction and allowing the reaction to take place, with a particular repeating unit, until a desired characteristic chain length, molecular weight, or number of repeating units is achieved,
10 then synthesizing a second block to a desired extent, and terminating the reaction or adding a third block or repeat of the first block, etc. With high-molecular weight systems, in order to achieve segregation into periodic, microphase-separated domains special processing steps may need to be taken. At higher molecular weights, a polymeric species may become more viscous, thus more time may be required for phase separation to occur. With high-molecular-weight systems, phase
15 segregation can be carried out by dissolving the system in a suitable solvent, removing the solvent slowly and, near the order-disorder transition point, greatly decreasing the rate of solvent removal and optionally adding kinetic energy by vibrating the system via an ultrasonic apparatus, imposing oscillatory or steady shear extensional flow, exposing the system to a static or dynamic electric or magnetic field (especially where one polymeric species or block has a higher relative susceptibility
20 to the field such as via incorporation of an auxiliary species) or combinations thereof or the like.

The size of separate polymeric domains can be controlled also via processes described above for adjustment of refractive index, such as incorporation of auxiliary particles, auxiliary homopolymeric species, auxiliary monomeric or cross-linkable species that are polymerized, grafted, and/or cross-linked in situ, and the like.

25 For purposes of the invention, a polymeric mixture or block copolymeric species having at least two polymeric blocks each comprised of species having a characteristic RMS chain length in a disordered state of from about 10 nm to about 2000 nm is desirable, or a polymeric mixture or block copolymeric species that self-assembles into a periodic structure having separate domains with characteristic dimensions of, in some embodiments from about 50 to about 1500 nm and in other
30 embodiments from about 300 to 5000 nm and in yet other embodiments from about 15 to 50 nm.

The periodic length L is the sum of all the lengths of the distinct dielectric domains contained in one period. For a particular embodiment for which a period contains two domains A and B (e.g. see Fig. 1), the periodic length $L = l_A + l_B$, where l_A and l_B are the characteristic dimensions of the A and B domains. In a particular embodiment for which both domains are defined by a pure A/B diblock copolymer with no additives, the periodic length is related to the RMS molecular chain length in the ordered state $L \propto (n_A + n_B)^{2/3} (\bar{x})$ where n_A and n_B are the respective number of monomer units of the separate polymer block copolymer blocks comprising the domains, and \bar{x} is the average length of the monomer repeat unit of the system, where the structure is ordered as a periodic, phase-separated structure. The relationship is $l_A + l_B = (n_A + n_B)^{1/2} (\bar{x})$ when the system is disordered. As previously discussed, for more complex systems, and systems with higher order dimensional periodicity, the relationship between the periodic length and the characteristic domain dimensions is more complex. These relationships can be used to assist selection of species for use in the invention. Typically, molecular weights of these species will be according to the preferred values noted above. In another embodiment, the periodic, phase-separated polymeric article includes separate domains each made up of at least about 1×10^3 monomer units per domain chain component, preferably at least 5×10^3 , and more preferably at least about 1×10^4 monomer units. This can be adjusted, however, to achieve the desired domain size where a particular domain includes repeating units of particularly high molecular weight, or including side groups that are relatively large and that thereby increase the size of the domain disproportionately to the number of repeat units.

A system can include, in addition to the polymeric species, solvent, preferably non-volatile, in an amount useful in swelling one or both domains, e.g. mineral oil in a polybutadiene/styrene copolymer which will swell the polybutadiene domain. This can be used to control the size of one or more domains. The system can also include other polymeric or non-polymeric additives for modification of domain dimension, dielectric constant/refractive index, or processibility. In addition, a suitable non-polymeric additive can also constitute a separate phase/domain within the photonic band gap structure.

A series of screening techniques can be used to select appropriate polymeric species for use in the polymeric, photonic band gap articles of the invention which include screening of constituent materials, process screening, and optical response screening. In a first test, an absorption measurement is carried out for each constituent of the final material, individually or in

combinations, which comprise the domain compositions (e.g. a homopolymer corresponding to each polymeric block type, pure crystallite film, or a combination). Also, a disordered arrangement of the polymeric species (block copolymeric species, mixture of homopolymeric species, etc.) is provided (an arrangement not phase-separated into domains with periodicity on the order of the wavelength of applied radiation) and irradiated to determine its degree of transparency. A material of a useable thickness that is sufficiently transparent and is not totally absorbent throughout the wavelength range of interest is potentially useful.

In another test, materials are selected for suitable dielectric constants. This test can entail performing index of refraction measurements, using an ellipsometer, on a thin film of a pure species or mixture defining a domain composition. The index of refraction of refraction can be determined using transmission or reflectivity measurements as a function of wavelength and comparing them to a desirable calculated response (Joannopolouus, et al.). The materials should also be screened for the ability to form structures with appropriate characteristic domain dimensions and periodic length scales. For embodiments using block copolymers, this can be done by measuring the molecular weight of the block copolymers using Nuclear Magnetic Resonance (NMR), Low Angle Laser Light Scattering, or Mass Spectrometry.

Planning and simple screening tests can be used to assess the relative compatibility of components including miscibility, phase separation, chemical stability, and processing stability in order to select suitable components for use as polymeric species 20 and 22, whether they be separate species, different blocks of a block copolymeric species, or a combination. A first and second species should be comprised of components that are immiscible at an appropriate molecular weight and composition. The χ parameter, which is extensively tabulated for a wide range of polymers, can be used to predict miscibility. Once a particular set of species is selected, they can be mixed (if not defined by a block copolymer) and screened for suitability for use in the invention by analysis via differential scanning calorimetry. If two glass transition temperatures are observed, then the two species (or two blocks of a block copolymer) are immiscible, that is, the desired phase separation has taken place. If only one glass transition temperature is observed, then the components are miscible and phase separation has not occurred, or the glass transition temperatures of the differing species or blocks are coincidentally similar. For the latter situation, if one glass transition temperature is observed, another screening test involving small angle scattering measurements can determine

whether phase separation has occurred. Melt temperature and the existence of crystallinity are readily determined by thermal analysis techniques such as DSC or DTA.

Another test involves subjecting the polymeric material or block copolymer to heat and determining the resistance to flow. If the material flows easily as a liquid, microphase separation and resulting dimensional stability at the test temperature does not exist.

Processing methods should also be screened for suitability with desired materials. For example, processing temperatures should be below degradation temperatures. Also, the types and magnitude of the physical forces applied during processing should be conducive to successful assembly of photonic band gap systems, and thus should be able to guide one or more assembly/partitioning events, which give rise to dielectric domains and a proper assembly of the domains into the periodic band gap structure. Processing methods should be avoided that lead to the proliferation of undesired imperfections or that induce undesired physical damage to the materials or structure. The formation of a periodic structure possessing suitable characteristic domain dimensions and periodic length and composition can be verified by small angle x-ray measurements (SAXS), transmission electron microscopy (TEM), optical microscopy, atomic force microscopy (AFM). These methods can also be used to inventory imperfections in the structure.

As another screening test, if creation of photonic band gap materials including phase-separated domains with periodicity on the order of the wavelength of the desired electromagnetic radiation is difficult, but fabrication of phase-separated articles including larger domains is simpler, then a band gap material including domains on the order of, for example, the wavelength of microwaves can be fabricated and tested to determine its properties. If a useful band gap material results, then the material can be adjusted for formation of phase-separated domains of characteristic dimension suitable for the radiation of interest. In some embodiments this characteristic dimension is on the order of 50-1500 nanometers. In other embodiments, the characteristic dimension is on the order of 15-50 nm, and in yet other embodiments, the characteristic dimension is on the order of 300 nm to 5000 nm. The ultimate screening test is the determination of the optical response of the assembled periodic structure and its usefulness as a photonic band gap article over the frequency range of interest. This can be done by comparing calculated and measured dispersion relations while taking proper account of the finite dimensions of the system.

Radiation-propagating or radiation-containing defects or single or multimode cavities can be

created in the polymeric, photonic band gap articles 10, 28, and 32 of the invention in a variety of ways. In one-dimensional periodic structures a change in refractive index of one lamellae, or a change in the dimensions of one layer, for example by inserting a layer of another material, or use of an ABC multiblock blended with an AC diblock - effectively creating one layer of B in the multiblock AC system, can be carried out. In two-dimensional structures a point defect can be created by removing a cylinder with a laser or adding latex cylinders before or during formation of the structure. With reference to the structure of Fig. 3, a defect can be created by removing, selectively (via irradiation, etching, or the like) a contiguous series of cylinders of polymeric species 22. A line defect can be formed in two-dimensional and three-dimensional structures by magnetically guiding a heated sphere through the material. A line defect also can be created by drilling a hole, for example using an intense laser beam. A point defect in a three-dimensional structure can be made by adding latex spheres where the size and the index of refraction of the sphere can be controlled. Plane defects can be formed by cutting a three-dimensional structure along a specific plane, rotating the two pieces, and rejoining them together. Cutting a along a specific plane, rotating the two pieces, and rejoining them together can also be used to create a composite structure with a higher effective dimensionality than the initial structure. For example the two-dimensional system shown in Fig. 3 can be bisected along one or more X-Z planes, the sections can then be rotated relative to each other by an angle θ (or different angles for different pairs of sections), and rejoined so that the cylinders 22 are no longer continuous across the planes of bisection (i.e. they are misaligned). This new system can now act as a three-dimensional photonic band gap structure. Point or line defects also can be created by manipulation of intersecting beams of radiation, for example laser beams, ion beams, electron beams, or the like, where the intersecting beams alter the structure enough to create a defect but, along regions of each beam other than the intersecting portions, a structure remains unchanged. In another technique, a hot magnetic particle can be guided through a structure to create a "burned" pathway that defines a defect by using an alternating current electrical field to heat the particle and steering the particle by use of a direct current or magnetic field.

Another technique for forming defects is via manipulation of processing procedures. For example, anisotropy may be induced in certain directions by applying an external field or by roll casting. Where the defects are point defects, for example by incorporation of an impurity into one or

both of the polymeric phases, or introduction of an impurity that will be pinned at polymeric phase interfaces, optionally followed by removal of the impurity via etching or the like, a single-mode resonant optical cavity is defined. A three-dimensional, polymeric photonic band gap structure with a point defect can be used to suppress or induce spontaneous emission from excited atoms placed in those defects. This can be used as a photonic bit or data storage item.

As mentioned above, a variety of polymeric species, including combinations of polymeric species, can be used to create the periodic polymeric photonic band gap structure of the invention. Where block copolymers are used, they can be linear block copolymers, "comb" copolymers, star copolymers, radial teleblock copolymers, dendrimers, or a combination. Those of ordinary skill in the art can select suitable polymers or combinations of polymers to create the phase-separated structure of the invention.

The function and advantage of these and other embodiments of the present invention will be more fully understood from the examples below. The following examples are intended to illustrate the benefits of the present invention, but do not exemplify the full scope of the invention.

Example 1: Formation of Polymeric Photonic Band Gap Article

This prophetic example describes how one would fabricate a polymeric photonic band gap article.

A block copolymeric species of methyltetracyclododecene (MTD) and [2,3-trans-bis((tert-butyl-amido)methyl)norborn-5-ene] [ZnPh_2] are synthesized as described in Sankaran, et al., *Chem Mater.*, 5, 1133 (1993), incorporated herein by reference. A ring-opening metathesis polymerization technique is used and the polymer is synthesized using an amount of precursor and for a length of time sufficient to create blocks each of approximately 500,000 Daltons in molecular weight. The reaction takes place in benzene, vacuum distilled from CaH_2 and stored over NaK and filtered through a sintered glass frit prior to use. The reaction is terminated with pentadiene.

Periodic structures of alternating separate copolymeric domains are created by casting from solution while, near the point of complete removal of benzene, the system is exposed to ultrasonification for approximately 10 hours while the remainder of the solvent is gradually removed. The polymeric structure then is exposed to H_2S vapors in a suitable solvent for a period of 20 hours. Following this reaction, the polymer is exposed to atmosphere and excess H_2S gas is allowed to dissipate for a period of time of 6-10 hours. The sample is further evacuated at 100°C

for 12 hours. The result is a phase-separated article including ZnS clusters in the nanometer size range in one domain selectively, the overall structure having a refractive index ratio between domains of approximately 1.5. If the particular requisite refractive index contrast is not achieved, another refractive index-adjusting species, such as an aqueous dye, is added. Characterization of the
5 resulting polymeric structure is carried out as follows. Molecular weight characterization uses gel permeation chromatography and light scattering. X-ray photoelectron spectroscopy is used to characterized the particulate structure, and NMR spectroscopy (including proton NMR) is used to characterize the block copolymer. A three-dimensional periodic structure results.

A linear defect is created in the structure by guiding a heated article through the structure, the
10 heat supplied by an alternating current field, and the particle being guided through the structure by a direct current field.

Example 2: Formation of a One-dimensional Polymeric Photonic Band Gap Article Comprising Alternate Layers of High and Low Index of Refraction

This example demonstrates the self assembly of a structure of periodically occurring first
15 and second separate dielectric domains in the presence of a flow field. The structure in this example exhibited one dimensional periodicity. The dielectric domains were present in a polymeric article constructed from a P2VP/PI/PS triblock copolymer and an auxiliary refractive index modifying species residing primarily in one of the domains. The domain characteristic size was approximately 20nm for the article fabricated according to this example for both the high and low dielectric
20 constant domains, and the refractive index ratio was estimated to be above 1.1. The fabrication procedure used in this example is general and can be used to fabricate a large number of potentially useful one, two and three dimensional periodic structures at different length scales and refractive indices. To demonstrate the flexibility of the procedure we chose to make a layered dielectric structure. The characteristic dielectric domain length scale was controlled in this example primarily
25 by the length of the block copolymer and by the volume of added auxiliary species. This length scale can be increased by using higher molecular weight polymers or via other methods described previously.

The structure was fabricated using a block copolymer and a dielectric constant enhancing additive. The block copolymer was comprised of poly-2 vinyl pyridine (P2VP), polyisoprene (PI),
30 and polystyrene (PS). The dielectric constant enhancing additive was comprised of CdSe crystallites

coated with a surface modifying group (tri-octyl phosphine oxide) that had an affinity to one of the blocks (P2VP). The CdSe crystallites were initially dispersed in tetrahydrofuran (THF) and were approximately 3 nm in diameter. The crystallites were prepared according to a procedure outlined in Murray et al. ("Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te)

5 Semiconductor Nanocrystallites". J. Am. Chem. Soc. 115, 8706, (1993)).

The articles were prepared as follows. To 2.4 ml of a THF solution of crystallites at a concentration of 0.1 mol/liter was added 0.6 g of PS/PI/P2VP triblock copolymer was added. The molecular weights of the blocks were 23,000 Da, 53,000 Da, and 23,000 Da for the PS, PI, and P2VP respectively. The total molecular weight of the block copolymer was chosen to give a
10 periodicity distance which corresponded to the desired optical band gap range.

The CdSe nanocrystallites, prepared according to the procedure of Murray et al, were coated with the bi-functional surface modifying group trioctyl phosphine oxide (TOPO). Each modifying group had a head group which bound or coordinated to the nanocrystallite surface and a tail which was miscible in one of the blocks (P2VP).

15 The block copolymer and the crystallites were mixed, roll cast at 40 RPM according to the procedure outlined in Albalak and Thomas (1993). The article was then annealed at 120 °C under vacuum for 48 hr yielding an article with a periodic dielectric structure.

The structure of the article was analyzed as follows. Portions of the article were thin sectioned using an ultra microtome and sections were transferred to 600 mesh copper grids.

20 The sections were stained for 1 minute in a iodine rich atmosphere followed by staining with osmium tetroxide (OsO_4) for contrast. TEM images of the sections were then obtained on a JEOL 2000 TEM at various magnifications.

The small angle x-ray diffraction(SAXS) pattern of the material was measured using a Rigaku 18KW rotating anode x-ray generator and a Seimens small angle diffractometer with
25 Seimens HI-STAR area detector.

The sample prepared as described above exhibited both nanocrystallite sequestering and long range order. The identification of the CdSe rich phase and the structure was conducted by TEM using a light Iodine staining (~1 minute) and OsO_4 staining of the sections. A typical electron photomicrograph of a section is shown in Fig. 6. The figure indicates that the system was a layered,
30 periodic structure with the trioctyl phosphine capped CdSe particles 25 sequestered into the Poly 2-

vinyl pyridine phase 26. The volume fraction of the particles in the sequestering phase was approximately 15%. The structure formed was a layered structure of ABCCBAABC type where B 27 was isoprene, A 29 was polystyrene, and C 26 was the CdSe-incorporating P2VP phase. The apparent reason for the sequestering of CdSe into the P2VP phase was the existence of a Lewis Base
5 nitrogen in that phase which coordinated to the surface of the CdSe particle. Pi-pi orbital interactions in the PS phase and the non-polarity of the PI phase did not favor the polar CdSe particle surfaces. The periodicity length was approximately 40nm. The long range order in this sample was achieved by a combination of roll casting and annealing at 120 °C for 48hr. Fig. 7 shows the SAXS pattern of the system as prepared indicating displaying a significant anisotropy
10 indicating a globally aligned structure.

Example 3: Formation of a Two Dimensional Periodic Band Gap Structure Consisting of High Dielectric Constant Cylinders on a Triangular Lattice in a Low Dielectric Constant Matrix.

This example demonstrates the self assembly of a structure of periodically occurring first and second separate dielectric domains in the presence of a flow field. The structure in this example
15 exhibited two dimensional periodicity. The dielectric domains were present in a polymeric article constructed from a PS/PI/PS triblock copolymer and an auxiliary refractive index modifying species, which were CdSe nanocrystals, residing primarily in one of the domains. The domain characteristic size was approximately 15nm for the article fabricated according to this example for both the high and low dielectric constant domains, and the refractive index ratio was estimated to be above 1.1.
20 The fabrication procedure used in this example is general and can be used to fabricate a large number of potentially useful one, two and three dimensional periodic structures with different length scales and refractive indices. To demonstrate the flexibility of the procedure we chose to make a layered dielectric structure. The characteristic dielectric domain length scale was controlled in this example primarily by the length of the block copolymer and by the volume of added auxiliary
25 species. This length scale can be increased by using higher molecular weight polymers or via other methods described previously. The dielectric contrast can be increased by increasing the volume of the auxiliary refractive index modifying species or by other means previously described.

The structure was fabricated using a block copolymer and a dielectric constant enhancing additive. The block copolymer comprised polystyrene (PS) and polyisoprene (PI) blocks. The
30 dielectric constant enhancing additive comprised CdSe crystallites coated with a surface modifying

group (tri-octyl phosphine oxide (TOPO)) which had an affinity to one of the blocks (in this case to the PS). The CdSe crystallites were initially dispersed in toluene and were approximately 3nm in diameter. The crystallites were prepared according to the procedure outlined in Murray et al. (1993).

The sample preparation procedure was as follows. 3.05nm diameter TOPO capped CdSe
5 crystallites in toluene were prepared according to Murray et al. (1993) at a concentration of approximately . 0.7g of DEXCO4211 SIS (11.7k-46k-11.7k) polymer was dissolved in 2 ml of toluene. To this solution was added 0.05g of amine terminated PS 2,600 Da (Polymersource, Quebec City, Canada). The solution was thoroughly mixed. The solution of CdSe crystallites in toluene was then added to the solution. The resulting material was then roll cast at 40 RPM and
10 annealed under vacuum for 72hr to produce the final polymeric article.

The structure of the article was analyzed by TEM and SAXS as previously described.

The resultant structure consisted of cylinders of PS in a matrix of PI. The CdSe particles were sequestered in the PS cylinders. A typical TEM photomicrograph of the structure is shown in Fig. 8 indicating that CdSe nanocrystals 30 sequestered in the PS rods 31, which were separated by
15 PI matrix 33. The amine terminated PS chains played an instrumental role in the sequestering process. Indeed, TOPO capped CdSe nanocrystallites are immiscible in a SIS triblock and will phase separate into micron-size clumps 30. The center to center distance between adjacent cylinders in this structure was approximately 27nm. The small angle scattering pattern (Fig. 9) displays an anisotropic horizontal diffraction peak pattern 34, corresponding to a triangular lattice, and an
20 isotropic scattering ring 35 corresponding to a single particle scattering on the outer edge of the ring and 35 particle diameter object on the inner. The effect of annealing on the long range order can be observed by comparing the number of diffraction orders present prior to annealing (Fig. 9) and after a 72 hr annealing period (Fig 10). There is little isotropic scattering at larger length scales this is in agreement with the sequestering event and the isolation of the sequestering phase. (I don't
25 understand this statement).

Example 4: Preparation of a One Dimensional Periodic Band Gap Structure Comprising Alternating Layers of High and Low Index of Refraction.

This prophetic example shows how one would fabricate a self assembled structure of periodically occurring first and second separate dielectric domains. Self assembly occurs in the
30 presence of a flow field. The structure in this example exhibits one dimensional periodicity. The

dielectric domains are present in a polymeric article constructed from a P2VP/PI/P2VP triblock copolymer and an auxiliary refractive index modifying species residing primarily in one of the domains. The domain characteristic size is approximately 400nm for the article fabricated according to this example for both the high and low dielectric constant domains, and the refractive index ratio is estimated to be above 1.1. The fabrication procedure used in this example is general and can be used to fabricate a large number of potentially useful one, two and three dimensional periodic structures with different length scales and refractive indices. In this prophetic example, we demonstrate how one would use the procedure to fabricate a one dimensional dielectric periodic structure. The characteristic dielectric domain length scale is controlled in this example primarily by the length of the block copolymer and by the volume of added auxiliary species. The length scales and dielectric contrast can be manipulated by means previously described.

The structures according to the present prophetic example are fabricated from a block copolymer and a dielectric constant-enhancing additive. The block copolymer is comprised of poly-2 vinyl pyridine (P2VP) and polyisoprene (PI). The dielectric constant-enhancing additive can be comprised of CdSe crystallites coated with a surface-modifying group (e.g. tri-octyl phosphine oxide (TOPO)) that is designed to have an affinity for one of the blocks of the block copolymer (for the case of TOPO-coated CdSe crystallites to the P2VP block). The CdSe crystallites, approximately 3 nm in diameter, are prepared according to the procedure given in Murray et al (1993) and are initially dispersed in tetrahydrofuran (THF).

The fabrication procedure of the polymeric band gap article proceeds as follows. An ABA-type triblock copolymer is synthesized or obtained (in other examples, a diblock or star or higher order block copolymer may be used) with 2 vinyl pyridine (P2VP) as block A and poly isoprene as block B. The molecular weights of the blocks are about 400 (kilograms/mol) for the poly-2-vinyl pyridine blocks (sum of two A blocks) and about 800 (kilograms/mol) for the poly isoprene block. These particular molecular weights are chosen to give alternate layers of P2VP and poly isoprene (PI) which yield a periodic structure with domain dimensions of 400nm useful as a band gap for radiation in the range near 2.5 μ m wavelength. The total molecular weight of the block copolymer is chosen to give a periodic length which is on the order of the wavelength in the material of the desired band gap 2.5/1.5.

Crystallites, which can comprise CdSe nanocrystallites or any other high dielectric crystallite

(such as CdTe AlTe GaAs and others), are synthesized or obtained that have an effective diameter that is smaller than the average domain size of the final polymer article. The nanocrystallites are coated with a surface modifying group, such as trioctyl phosphine oxide or other surface modifiers having a bi-functional chemical structure including a head group, which binds to or coordinates with the nanocrystallite surface, and a tail which is miscible in one of the blocks of the copolymer. The volume of the nanocrystallites added is chosen so that upon sequestering into one of the domains, the effective index of refraction of that domain is enhanced to a desired value and a desired morphology is attained. For example, adding 0.5 ml of CdTe crystallites with an index of refraction of $n=3.05$ at $0.55\mu\text{m}$ wavelength to 0.5ml of P2VP with an index of refraction of about 1.5 at $0.55\mu\text{m}$ will yield an effective index of refraction for the mixture of about $n=2.28$. The index of the sequestering phase can be increased by increasing the volume fraction of nanocrystallites or by choosing crystallites of higher index of refraction at the wavelength of interest. The volume of nanocrystallites chosen in this specific example (to give layers) should equal approximately the volume of the P2VP. The volume of the crystallites can be determined from their density and their molar concentration and weight.

The block copolymer and the crystallites are then mixed and a processing method is chosen that will enable removal of the solvent and aid formation of long range order. For example, the sample can be roll cast using the procedure outlined in Albalak et al. Or roll cast and annealed in a vacuum oven (for at least a few hours to a few days) with the temperature set at above the T_g of the two blocks. Alternatively, the sample can be evaporation cast onto a substrate with a surface treated to be preferentially interact with one of the blocks. For example, a glass surface can be used that has been dipped in Hexamethyldisilazane making it preferential interact with the PI block. Using the procedure above, a periodic dielectric lattice can be synthesized with a structure similar to that shown in Fig. 6 SAXS pattern similar to that shown in Fig. 7.

Example 5: Preparation of a Two Dimensional Periodic Band Gap Structure Comprising Cylinders With Relatively High Effective Index of Refraction Oriented on a Triangular Lattice in a Matrix With Relatively Low Effective Index of Refraction.

This prophetic example shows how one would fabricate a self assembled structure of periodically occurring first and second separate dielectric domains arranged to exhibit two-dimensional periodicity with self assembly occurring in the presence of a flow field. As in prophetic

example 4, the dielectric domains are present in a polymeric article constructed from a P2VP/PI/P2VP triblock copolymer and an auxiliary refractive index modifying species residing primarily in one of the domains. The domain characteristic size would be approximately 200nm for the high dielectric constant cylindrical domains with a center-to-center spacing of about 400 nm.

5 The refractive index ratio is estimated to be above 1.1. The fabrication procedure used in this example is a modification of that described in example 4 and is general and can be used to fabricate a large number of potentially useful one, two and three dimensional periodic structures with different length scales and refractive indices. In this prophetic example, we demonstrate how one would use the procedure to fabricate two dimensional dielectric periodic structures comprised of
10 cylinders on a triangular lattice. The characteristic dielectric domain length scale is controlled in this example primarily by the length of the block copolymer and by the volume of added auxiliary species. The length scales and dielectric contrast can be manipulated by means previously described.

The structure according to the current prophetic example is fabricated from an ABA type
15 triblock copolymer with P2VP comprising block A and PI comprising block B. The fabrication procedure is similar to that outlined in example 4 including the following modifications. The molecular weights of the blocks are about 280 (kilograms/mol) for the poly-2-vinyl pyridine blocks (sum of the two A's) and about 1300 (kilograms/mol) for the polyisoprene block. These particular molecular weights are chosen to yield a structure comprising cylinders of P2VP in a matrix of
20 polyisoprene (PI). These particular molecular weights are chosen to yield cylinders of P2VP in a matrix of poly isoprene (PI) which yield a periodic structure with domain dimensions of 100nm useful as a band gap for radiation in the wavelength range near 200nm. The total molecular weight of the block copolymer is chosen to give a periodic length of about 400nm which is on the order of the wavelength range of the desired band gap.

25 The crystallites in the current example are coated with TOPO and sequester into the P2VP phase. In addition, the volume of nanocrystallites chosen in this specific example (to give cylinders) should be such that the volume fraction of the combined phase comprising P2VP and crystallites is between approximately 0.2 and 0.32 based on the total volume of the system (P2VP+crystallites and PI).

30 Example 6: Preparation of a Three Dimensional Periodic Band Gap Structure Comprising a Double

Gyroid.

This prophetic example shows how one would fabricate a self assembled structure of periodically occurring first and second separate dielectric domains arranged to exhibit three-dimensional periodicity with self assembly occurring in the presence of a flow field. In the present example, the dielectric domains are present in a polymeric article constructed from a PS/PI/P2VP triblock copolymer and an auxiliary refractive index modifying species residing primarily in one of the domains. The domain characteristic size would be approximately 100nm for the high dielectric constant domains and 300nm for the low dielectric constant domains. The refractive index ratio is estimated to be above 1.1. The fabrication procedure used in this example is a modification of that described in example 4 and is general and can be used to fabricate a large number of potentially useful one, two and three dimensional periodic structures with different length scales and refractive indices. In this prophetic example, we demonstrate how one would use the procedure to fabricate three-dimensional dielectric periodic structures comprising a double gyroid configuration. The characteristic dielectric domain length scale is controlled in this example primarily by the length of the block copolymer and by the volume of added auxiliary species. The length scales and dielectric contrast can be manipulated by means previously described.

The structure according to the current prophetic example is fabricated from an ABC type triblock copolymer with P2VP comprising block A, PI comprising block B, and polystyrene (PS) comprising block C. The fabrication procedure is similar to that outlined in example 4 including the following modifications. The molecular weights of the blocks are about 100 (kilograms/mol) for the poly-2-vinyl pyridine blocks (block A), about 800 (kilograms/mol) for the polyisoprene block (Block B), and about 200 (kilograms/mol) for the polystyrene block (Block C). These particular molecular weights are chosen to yield a structure comprising a double gyroid, with P2VP and PS each forming separate continuous phases within a matrix of PI. These particular molecular weights are chosen to yield a periodic double gyroid structure.

The crystallites in the current example are coated with TOPO and sequester into the P2VP phase. In addition, the volume of nanocrystallites chosen in this specific example, for a double gyroid structure, should be such that the volume fraction of the combined glassy phases (P2VP+crystallites and the separate PS phase) is between approximately 0.32 and 0.37 based on the total volume of the system (P2VP+crystallites and PS and PI).

Example 7: Preparation of a One Dimensional Periodic Band Gap Structure Comprising Alternating Layers of High and Low Index of Refraction.

This prophetic example shows how one would fabricate a self assembled structure of periodically occurring first and second separate dielectric domains arranged to exhibit one-dimensional periodicity with self assembly occurring in the presence of a flow field. In the present example, the dielectric domains are present in a polymeric article constructed from a PS/PI/PS triblock copolymer and an auxiliary refractive index modifying species residing primarily in one of the domains. The domain characteristic size would be approximately 400nm for the high and low dielectric constant domains (layers). The refractive index ratio is estimated to be above 1.1. The fabrication procedure used in this example is a modification of that described in example 4 and is general and can be used to fabricate a large number of potentially useful one, two and three dimensional periodic structures with different length scales and refractive indices. The characteristic dielectric domain length scale is controlled in this example primarily by the length of the block copolymer and by the volume of added auxiliary species. The length scales and dielectric contrast can be manipulated by means previously described.

The structure according to the current prophetic example is fabricated from an ABA type triblock copolymer with PS comprising block A and PI comprising block B. The fabrication procedure is similar to that outlined in example 4 including the following modifications. The molecular weights of the blocks are about 800 (kilograms/mol) for the PS blocks (sum of the two A's) and about 800 (kilograms/mol) for the PI block. These particular molecular weights are chosen to give alternate layers of P2VP and poly isoprene (PI) which yield a periodic structure with domain dimensions of 400nm useful as a band gap for radiation in the wavelength range around 2.5 μ m.. The total molecular weight of the block copolymer is chosen to give a periodic length which is on the order of the wavelength range 2.5/1.5 of the desired band gap.

The crystallites in the current example are coated with a bi-functional surface modifying group, such as amine- or thiol-terminated polystyrene which have preferential affinity for the PS and thus sequester into the PS phase. The volume of the nanocrystallites added is chosen so that upon sequestering into one of the domains, the effective index of refraction of that domain is enhanced to a desired value and a desired morphology is attained. For example, adding 0.5 ml of pure CdTe crystallites with an index of refraction of $n=3.05$ at a wavelength of about 0.55 μ m to 0.5ml of PS

with an index of refraction of about 1.5 at 0.55 μm will yield an effective index of refraction for the mixture of about $n=2.28$. The index of the sequestering phase can be increased by increasing the volume fraction of nanocrystallites or by choosing crystallites of higher index of refraction at the wavelength of interest. In addition, the volume of nanocrystallites chosen in this specific example

(to give a layered structure) should equal approximately the volume of the PS.

Example 8: Preparation of a Two Dimensional Periodic Band Gap Structure Comprising Cylinders With Relatively High Effective Index of Refraction Oriented on a Triangular Lattice in a Matrix With Relatively Low Effective Index of Refraction.

This prophetic example shows how one would fabricate a self assembled structure of periodically occurring first and second separate dielectric domains arranged to exhibit two-dimensional periodicity with self assembly occurring in the presence of a flow field. In the present example, the dielectric domains are present in a polymeric article constructed from a PS/PI/PS triblock copolymer and an auxiliary refractive index modifying species residing primarily in one of the domains. The domain characteristic size would be approximately 200nm for the high dielectric constant cylinders with a center-to-center distance between cylinders of about 400nm. The refractive index ratio is estimated to be above 1.1. The fabrication procedure used in this example is a modification of that described in example 7 and is general and can be used to fabricate a large number of potentially useful one, two and three dimensional periodic structures with different length scales and refractive indices. In this prophetic example, we demonstrate how one would use the procedure to fabricate two dimensional dielectric periodic structures comprised of cylinders on a triangular lattice. The characteristic dielectric domain length scale is controlled in this example primarily by the length of the block copolymer and by the volume of added auxiliary species. The length scales and dielectric contrast can be manipulated by means previously described.

The structure according to the current prophetic example is fabricated from an ABA type triblock copolymer with PS comprising block A and PI comprising block B. The fabrication procedure is similar to that outlined in example 7 with the following modifications. The molecular weights of the blocks are about 280 (kilograms/mol) for the PS blocks (sum of the two A's) and about 1291 (kilograms/mol) for the PI block. These particular molecular weights are chosen to yield a structure comprising cylinders of PS in a matrix of PI. These particular molecular weights are chosen to yield cylinders of PS in a matrix of PI which yield a periodic structure with domain

dimensions of 100nm and 200nm useful as a band gap for radiation in the wavelength range around 300nm.. The total molecular weight of the block copolymer is chosen to give a periodic length which is on the order of the wavelength range (around 300nm) of the desired band gap.

The crystallites in the current example are coated with amine- or thiol-terminated polystyrene and sequester into the PS phase. In addition, the volume of nanocrystallites chosen in this specific example (to give a triangular lattice of cylinders) should be such that the volume fraction of the combined phase comprising PS and crystallites is between approximately 0.2 and 0.32 based on the total volume of the system (PS+crystallites and PI).

10 Example 9: Preparation of a Three Dimensional Periodic Band Gap Structure Comprising a Double Gyroid.

This prophetic example shows how one would fabricate a self assembled structure of periodically occurring first and second separate dielectric domains arranged to exhibit three-dimensional periodicity. In the present example, the dielectric domains are present in a polymeric article constructed from a PS/PI/PMMA triblock copolymer and an auxiliary refractive index modifying species residing primarily in one of the domains. The domain characteristic size would be approximately 100nm for the high and 300nm for the low dielectric constant domains respectively. The refractive index ratio is estimated to be above 1.1. The fabrication procedure used in this example is a modification of that described in example 7 and is general and can be used to fabricate a large number of potentially useful one, two and three dimensional periodic structures with different length scales and refractive indices. In this prophetic example, we demonstrate how one would use the procedure to fabricate three-dimensional dielectric periodic structures comprising a double gyroid configuration. The characteristic dielectric domain length scale is controlled in this example primarily by the length of the block copolymer and by the volume of added auxiliary species. The length scales and dielectric contrast can be manipulated by means previously described.

The structure according to the current prophetic example is fabricated from an ABC type triblock copolymer with PS comprising block A, PI comprising block B, and polymethylmethacrylate comprising block C. The fabrication procedure is similar to that outlined in example 7 including the following modifications. The molecular weights of the blocks are about 100 (kilograms/mol) for the PS block (Block A), about 800(kilograms/mol) for the PI block (Block B),

and about 200 (kilograms/mol) for the PMMA block (Block C). These particular molecular weights are chosen to yield a structure comprising a double gyroid with PS and PMMA each forming separate continuous phases within a matrix of PI. These particular molecular weights are chosen to yield a periodic double gyroid structure.

5 The crystallites in the current example are coated with amine- or thiol-terminated polystyrene and sequester into the PS phase. In addition, the volume of nanocrystallites chosen in this specific example, for double gyroid structure, should be such that the volume fraction of the combined glassy phases (PS+crystallites and the separate PMMA phase) is between approximately 0.32 and 0.37 based on the total volume of the system (PS+crystallites and PMMA and PI).

10 Example 10: Band gap structures Fabricated With Ozonolysis of the PI Phase

To any of the above examples an additional step can be added that includes the ozonolysis of the PI phase according to the method described in Hashimoto et al 1997, Langmuir vol 13, pp 6869-6872 incorporated herein by reference. This ozonolysis step enhances the dielectric contrast by selectively removing the PI phase from the structure. Air-filled cylinders arranged on a triangular
15 lattice can be created using a PI/PS/PI triblock copolymer with a total molecular weight of 2×10^6 Da with volume fractions of 0.125/75/0.125 for the respective components. The triblock copolymer is dissolved in toluene and amine terminated PS coated Indium Phosphide ($n=4$) crystallites are added to the solution. The volume of the added crystallites should be equal to the volume of the PS. The solution then can be roll cast and annealed under vacuum for 48hr and subsequently subjected to
20 ozonolysis in order to remove the PI phase. The resultant structure will have a complete band gap 36 as predicted by Joannopolous et al. and as seen in Fig. 11.

Example 11: Band Gap Structures Fabricated With Nucleation of Gas Bubbles in One of the Phases.

To any of the above examples an additional fabrication step can be added in which a low molecular weight component, such as mineral oil with gas dissolved in it, is added to the block
25 polymer mixture. The mineral oil has selective affinity for the PI block and will tend to swell it. By decreasing the pressure in the vessel containing the mixture to about 10^{-3} torr in combination with sonification gas bubbles will nucleate in the PI phase thus lowering its effective index of refraction.

In all of proceeding examples involving fabrication of photonic band gap articles including an elastic domain, such as a domain comprised of polyisoprene (PI). The elasticity of the PI phase
30 will allow the resulting structure to undergo deformation upon application of stress thus allowing

adjustment of the periodic length of the periodic structure and the band gap frequency of the article. The periodic length may be increased in these structures by as much as 1000 % due to imposition of physical stress (Honeker et al. "Chemistry of Materials" vol 8 p. 1702 (1996)) enabling formation of band gap articles useful for inhibiting radiation over a very wide range of free space wavelength up
5 to 50 μ m.

Those skilled in the art would readily appreciate that all parameters listed herein are meant to be exemplary and that actual parameters will depend upon the specific application for which the methods and apparatus of the present invention are used. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the
10 appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described. Also within the scope of the present invention are photonic band gap systems derived from any combinations of the systems previously described.

What is claimed is:

CLAIMS

1. A system comprising:

a polymeric article including a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain each having a characteristic dimension of from about
5 50 nm to about 1,500 nm and having a refractive index ratio of at least about 1.1 for a continuous set of wavelengths lying within a range of from about 100 nm to about 10 microns.

2. A system comprising:

a polymeric article including a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain each having a characteristic dimension of from about
10 15 nm to about 50 nm and having a refractive index ratio of at least about 1.2 for a continuous set of wavelengths lying within a range of from about 50 nm to about 1000 nm.

3. A system comprising:

a polymeric article including a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain each having a characteristic dimension of from about
15 300 nm to about 5000 nm and having a refractive index ratio of greater than 1.0 for a continuous set of wavelengths lying within a range of from about 400 nm to about 50 microns.

4. A system comprising a structurally periodic polymeric structure including a defect in periodicity being at least partially transparent to electromagnetic radiation in a wavelength range of from about 100 nm to about 50 microns, and a portion surrounding the defect, the portion surrounding the
20 defect being reflective to the electromagnetic radiation.

5. A system comprising a polymeric article including a three-dimensional periodic variation in the refractive index.

6. A method comprising:

exposing a portion of a polymeric article in an ordered state, having a path length, to
25 electromagnetic radiation within a free space wavelength range of from about 50 nm to about 50 microns and allowing the article to inhibit transmittance of the electromagnetic radiation to an extent greater than the article in a disordered state has the ability to inhibit transmittance of the electromagnetic radiation at the frequency through the path length.

7. A method comprising:

30 creating a defect in a polymeric article including a periodic structure of a plurality of periodically

occurring separate domains by inserting into the material a plane of a material different from materials defining the polymeric article prior to creation of the defect.

8. A method comprising:

creating a defect in a polymeric article including a periodic structure of a plurality of periodically occurring separate domains by altering polymeric material in the article.

9. A method as in claim 8, comprising removing polymeric material via irradiation.

10. A method as in claim 8, comprising exposing the material to intersecting beams of radiation.

11. A method as in claim 8, comprising removing the material via etching.

12. A method comprising:

creating a defect in a polymeric article including a periodic structure of a plurality of periodically occurring separate domains by magnetically guiding a heated object through the article.

13. A system or method as in any preceding claim, the polymeric article including a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain each having a characteristic dimension, at least one of the first and second domains containing an auxiliary refractive index modifier providing the first and second domains with a refractive index ratio of greater than 1.0 for the continuous set of wavelengths.

14. A system or method as in claim 13, at least one of the first and second domains containing an auxiliary refractive index modifier providing the first and second domains with a refractive index ratio of at least about 1.1 for the continuous set of wavelengths.

15. A system or method as in claim 13, at least one of the first and second domains containing an auxiliary refractive index modifier providing the first and second domains with a refractive index ratio of at least about 1.2 for the continuous set of wavelengths.

16. A system or method as in claim 13, at least one of the first and second domains containing an auxiliary refractive index modifier providing the first and second domains with a refractive index ratio of at least about 1.3 for the continuous set of wavelengths.

17. A system or method as in claim 13, at least one of the first and second domains containing an auxiliary refractive index modifier providing the first and second domains with a refractive index ratio of at least about 1.4 for the continuous set of wavelengths.

18. A system or method as in any preceding claim, wherein the article has an at least one-

dimensional periodic structure.

19. A system or method as in any preceding claim, wherein the article has an at least two-dimensional periodic structure.

20. A system or method as in any preceding claim, wherein the polymeric article includes
5 a period structure of a plurality of periodically occurring separate domains, with at least a first and a second domain formed by self-assembly of polymeric material.

21. A system or method as in any preceding claim, wherein the polymeric article includes a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain each having a characteristic dimension, wherein the first domain is polymeric and the
10 second domain is a non-polymeric material and the first and second domains are formed by polymeric self-assembly of the first domain and a polymeric precursor of the second domain followed by replacement of the precursor by the non-polymeric material.

22. A system or method as in the preceding claim, wherein the polymeric article includes a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a
15 second domain each having a characteristic dimension, comprising a block copolymer having at least two blocks A and B that are assembled into the first and second domains respectively.

23. A system or method as claim 22, wherein the block copolymer has at least three blocks A, B, and C.

24. A system or method as in any preceding claim, the polymeric article including a periodic
20 structure of the plurality of periodically occurring separate domains, with at least a first and a second domain each having a characteristic dimension, at least one of the first and second domains containing an auxiliary refractive index modifier providing the first and second domains with a refractive index ratio of at least about 2.0 for the continuous set of wavelengths.

25. A system or method as in any preceding claim, the polymeric article including a periodic
25 structure of the plurality of periodically occurring separate domains, with at least a first and a second domain each having a characteristic dimension, at least one of the first and second domains containing an auxiliary refractive index modifier providing the first and second domains with a refractive index ratio of at least about 4.0 for the continuous set of wavelengths.

26. A system or method as in any preceding claim, wherein the article has an at least three-
30 dimensional periodic structure.

27. A system as in claim 16, wherein the polymeric article includes at least one defect in periodicity.

28. A system or method as in any preceding claim, wherein the polymeric article includes a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain each having a characteristic dimension, wherein the polymeric article has an at least two-dimensional periodic structure and includes at least one defect in the periodic structure in at least one of the at least two dimensions.

29. A system as in claim 28, wherein the defect in periodicity is a series of interconnected points.

10 30. A system as in claim 28, wherein the defect is a line defect having a width and a length at least 5 times the width.

31. A system or method as in any preceding claim, wherein the polymeric article includes a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain each having a characteristic dimension, wherein the polymeric article has an at least three-dimensional periodic structure and includes at least one defect in the periodic structure in at least one of the at least three dimensions.

32. A system or method as in any preceding claim, wherein the polymeric article includes a defect in periodicity that is continuous pathway having a width and a length at least 10 times the width.

20 33. A system or method as in claim 32, wherein the continuous pathway is nonlinear.

34. A system as in claim 32, wherein the continuous pathway is three-dimensionally nonlinear.

35. A system or method as in any preceding claim, wherein the polymeric structure includes a plurality of periodically occurring separate domains, with at least a first and a second domain each having a characteristic dimension, the article including a defect in the order of the dielectric domains of the structure.

36. A system or method as in any preceding claim, wherein the polymeric structure includes a plurality of periodically occurring separate domains, with at least a first and a second domain each having a characteristic dimension, the article including a defect in refractive index between at least two adjacent domains.

37. A system or method as in any preceding claim, wherein the polymeric article includes a periodic structure of a plurality of periodically occurring separate domains with at least a first and a second domain, one of the first or second domains including an auxiliary refractive index-modifying species comprising particulate material.

5 38. A system or method as in any preceding claim, wherein the polymeric article includes a periodic structure of a plurality of periodically occurring separate domains with at least a first and a second domain, one of the first or second domains including an auxiliary refractive index-modifying species comprising a metal-containing, ceramic, or semi-conductor particulate material.

10 39. A system or method as in claim 37, wherein the refractive index-modifying species comprises polymeric particles.

40. A system as in claim 37, wherein the refractive index-modifying species comprises dye.

41. A system or method as in any preceding claim, the polymeric article comprising a periodic arranged structure of a plurality of separate domains wherein the structure inhibits transmittance of electromagnetic radiation at a free space wavelength range of from about 50 nm to about 50 microns
15 relative to transmission of electromagnetic radiation at the wavelength through a system comprised of the same materials but in a disarranged state.

42. A system or method as in claim 41, comprising a periodic arranged structure of a plurality of separate domains wherein the structure inhibits transmittance of electromagnetic radiation at a free space wavelength range of from about 300 nm to about 50 microns relative to transmission of
20 electromagnetic radiation at the wavelength through a system comprised of the same materials but in a disarranged state.

43. A system or method as in any preceding claim, comprising a periodic arranged structure of a plurality of separate domains wherein the structure has a photonic band gap in at least one direction within a free space wavelength range of from about 50 nm to about 50 microns.

25 44. A system or method as in claim 43, comprising a periodic arranged structure of a plurality of separate domains wherein the structure has a photonic band gap in at least one direction within a free space wavelength range of from about 300 nm to about 50 microns.

45. A system or method as in any preceding claim, wherein the polymeric article is an arranged, periodic structure of a plurality of periodically-occurring separate domains and the article, in
30 a disarranged state, is more transparent to light within a wavelength range of from about 100 nm to

about 10 microns.

46. A system or method as in claim 45, wherein the article, in a disarranged state, is at least partially transparent to light within a wavelength range of from about 400 nm to about 50 microns.

47. A system comprising:

5 a block copolymeric species having at least two blocks A and B, the blocks A and B being incompatible with each other such that the block copolymeric species is self-assembleable into a periodic structure of a plurality of at least first and second, separate domains each defined by association of similar blocks of the copolymeric species able to contain at least one auxiliary index of refraction enhancing additive, such that the first and second domains have a refractive index ratio of at least 1.1
10 at a wavelength within a range of from about 100 nm to about 10 microns.

48. A system comprising:

a block copolymeric species having at least two blocks A and B, each of the blocks A and B having a disordered characteristic length of from about 50 nm to about 2,000 nm, the blocks A and B being incompatible with each other such that the block copolymeric species is self-assembleable into a
15 periodic structure of a plurality of at least first and second, separate domains each defined by association of similar blocks of the copolymeric species able to contain at least one index of refraction enhancing additive, such that the first and second domains have a refractive index ratio of at least 1.1 at a wavelength within a range of from about 100 nm to about 10 microns.

49. A system as in claims 4-6, the block copolymer having a molecular weight of at least
20 about 80,000 Daltons.

50. A system as in claim 49, the block copolymer having a molecular weight of at least about 500,000 Daltons.

51. A system as in claim 50, the block copolymer having a molecular weight of at least about 2,000,000 Daltons.

25 52. A system or method as in any preceding claim, the polymeric article including periodicity in structure of a dimension on the order of from about 100 nm to about 50 microns.

53. A system comprising a polymeric photonic band gap structure.

54. A system as in claim 53, comprising a polymeric three-dimensional photonic band gap structure.

30 55. A method comprising:

processing a block copolymer to produce a phase-separated polymeric multi-domain structure including a periodic variation in the refractive index of a dimension on the order of from about 100 nm to about 50 microns to the extent that the article defines a photonic band gap structure.

5 56. A method as in claim 55, comprising allowing the block copolymer to self-assemble into the phase-separated polymeric multi-domain structure.

57. A method as in claim 56, comprising allowing the block copolymer to self-assemble into the phase-separated polymeric multi-domain structure in the presence of an applied electric, magnetic or mechanical flow field.

10 58. A method as in claim 57, comprising allowing the block copolymer to self-assemble into the phase-separated polymeric multi-domain structure in the presence of an applied electromagnetic field.

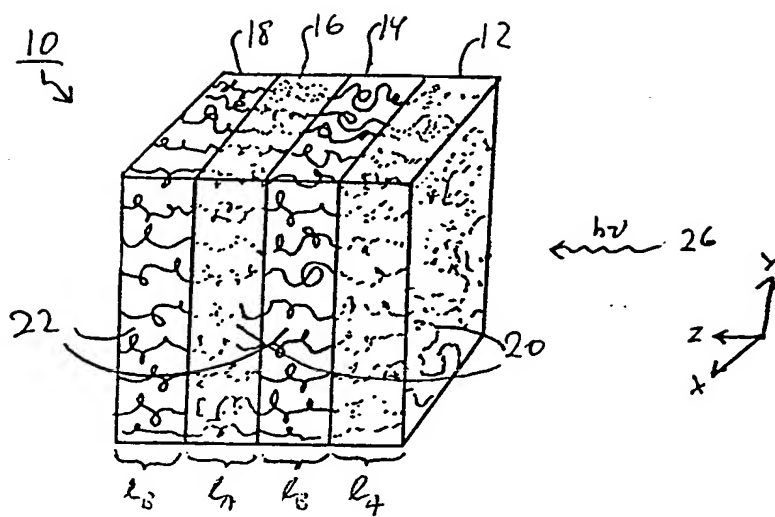


FIG. 1

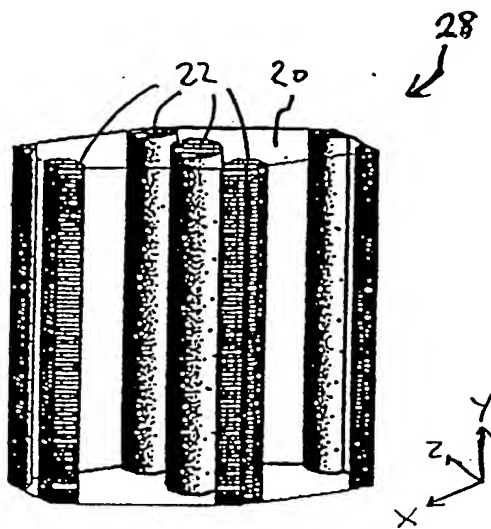


FIG. 3

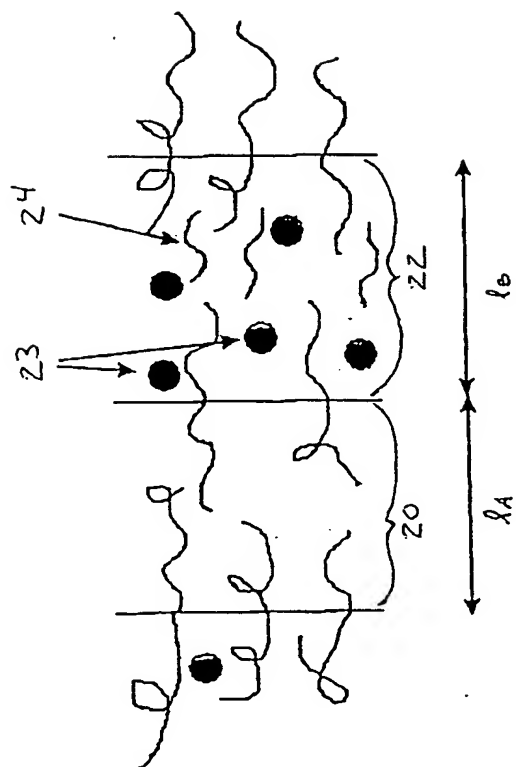


FIG. 2

3/7

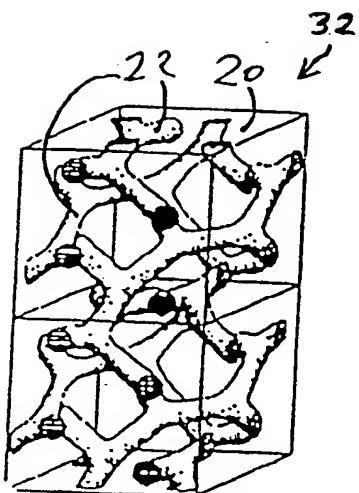


FIG. 4

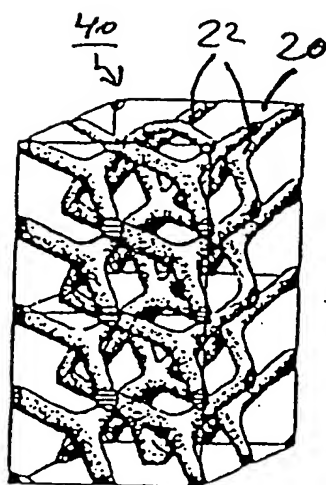


FIG. 5

4/7

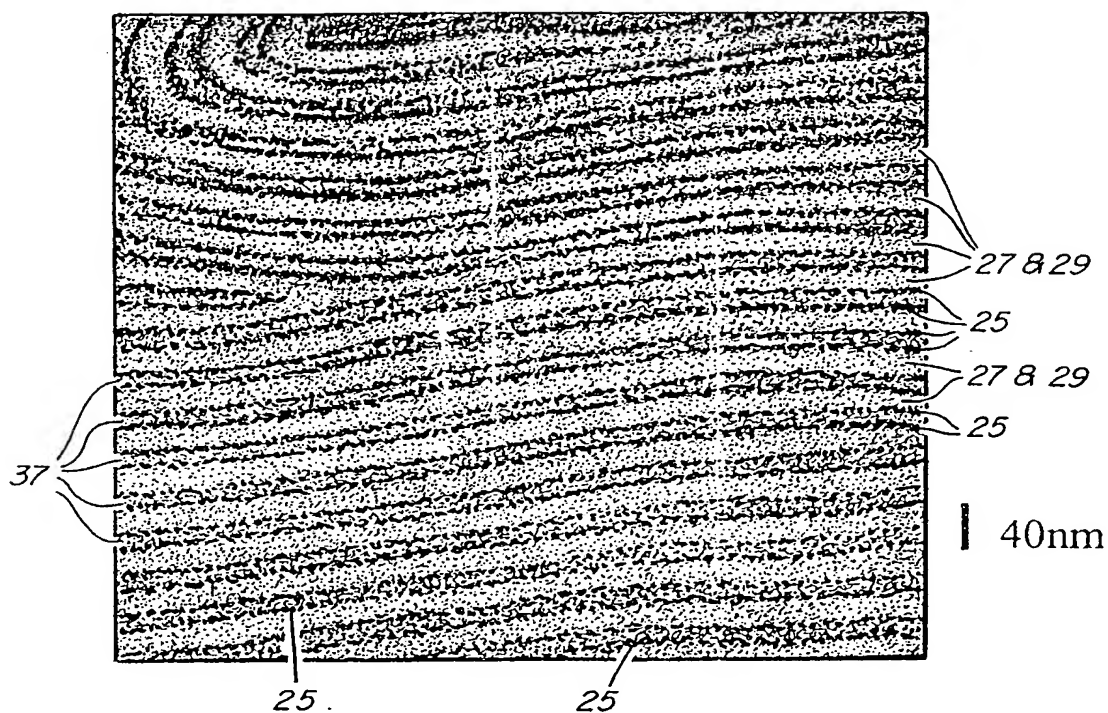


FIG. 6

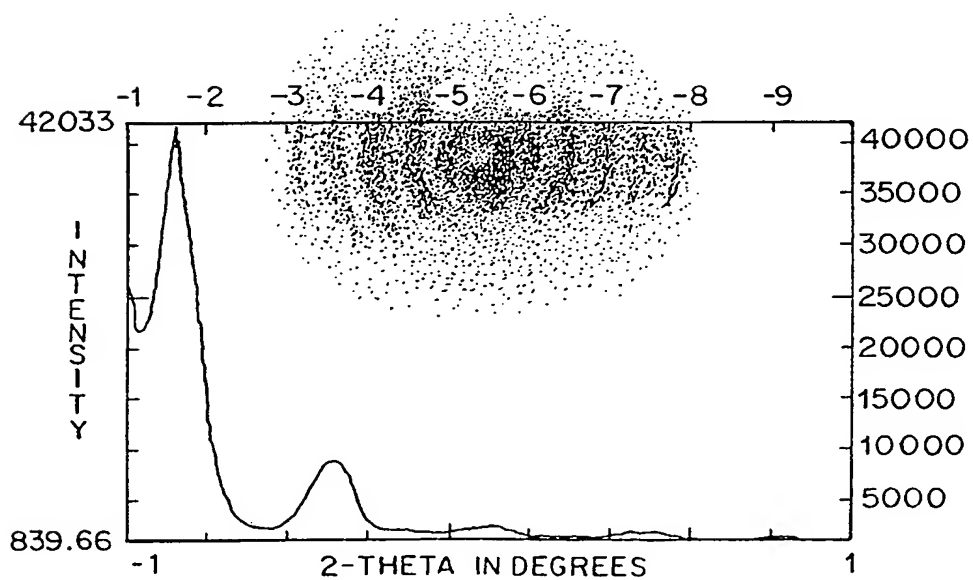


FIG. 7

RECTIFIED SHEET (RULE 91)
ISA/EP

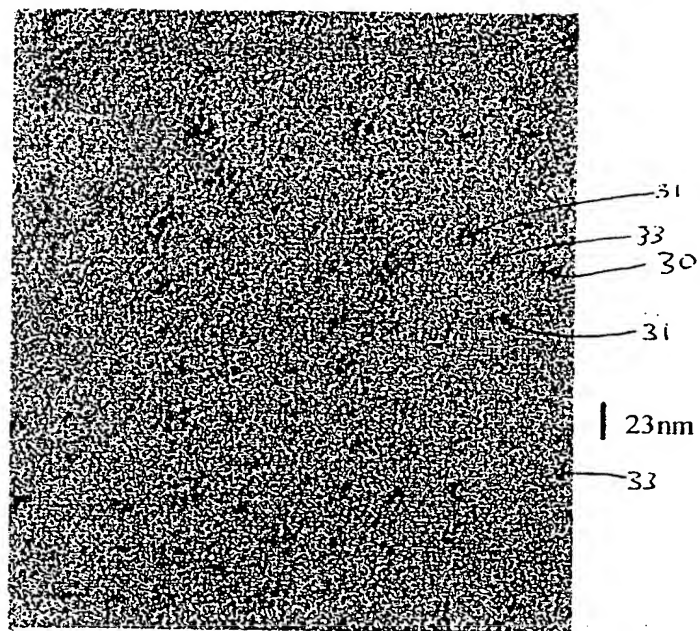


FIG 8

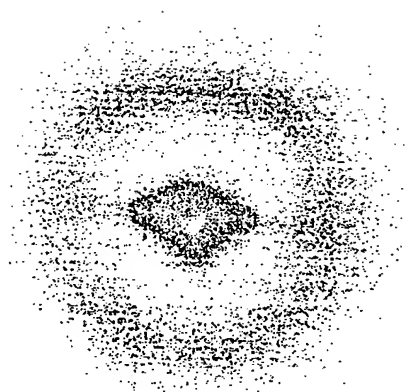


FIG. 9

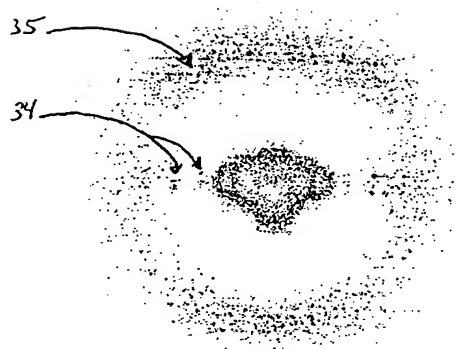
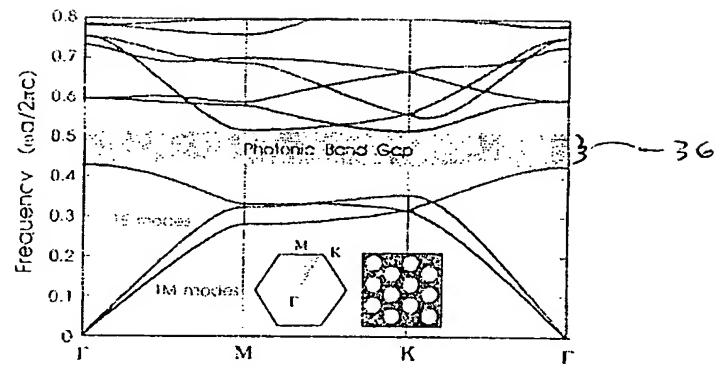


FIG. 10

7/7

FIG. 11

INTERNATIONAL SEARCH REPORT

national Application No
PCT/US 98/02974

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G02B6/138

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 600 483 A (FAN SHANHUI ET AL) 4 February 1997 see abstract; figure 1 see column 2, line 56 - column 3, line 4 see claims 1,27 ---	1-5,7,8, 53
A	WO 96 27225 A (MASSACHUSETTS INST TECHNOLOGY) 6 September 1996 see abstract; figures 3,4 see page 3, line 9 - line 18 see page 3, line 33 - page 4, line 2 see page 5, line 8 - line 21 ---	1-5,7-9, 53,55
A	US 5 471 180 A (BROMMER KARL ET AL) 28 November 1995 see abstract see column 2, line 17 - line 32 see column 4, line 21 - line 33 ---	1-5,7-9, 53,55
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
S" document member of the same patent family

Date of the actual completion of the international search

29 May 1998

Date of mailing of the international search report

19/06/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Jakober, F

INTERNATIONAL SEARCH REPORT

national Application No
PCT/US 98/02974

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 29621 A (MASSACHUSETTS INST TECHNOLOGY) 26 September 1996 see abstract; figures 3,8 see page 1, line 25 - page 3, line 14 see page 7, line 28 - page 8, line 12 -----	1-5,7,8, 53
A	ALBALAK, RAMON J.; THOMAS EDWIN, L.: "MICROPHASE SEPARATION OF BLOCK COPOLYMER SOLUTIONS IN A FLOW FIELD" JOURNAL OF POLYMER SCIENCE: PART B (POLYMER PHYSICS), vol. 31, no. 1, January 1993, pages 37-46, XP002066563 cited in the application see abstract see page 1, paragraph 1 -----	1-3,47, 48,55
A	US 5 385 114 A (MILSTEIN JOSEPH B ET AL) 31 January 1995 see the whole document -----	1-8,12, 53

INTERNATIONAL SEARCH REPORT

national Application No
PCT/US 98/02974

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5600483 A	04-02-1997	US 5440421 A WO 9530917 A	08-08-1995 16-11-1995
WO 9627225 A	06-09-1996	NONE	
US 5471180 A	28-11-1995	US 5187461 A AU 1435192 A WO 9215124 A US 5389943 A	16-02-1993 15-09-1992 03-09-1992 14-02-1995
WO 9629621 A	26-09-1996	NONE	
US 5385114 A	31-01-1995	US 5651818 A US 5688318 A	29-07-1997 18-11-1997

CORRECTED
VERSION*

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



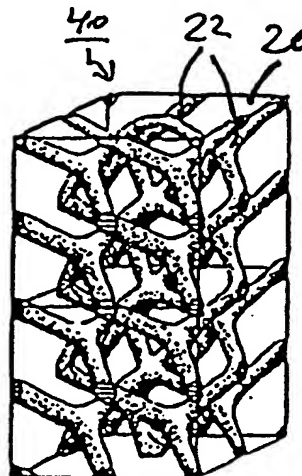
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: G02B 6/138	A1	(11) International Publication Number: WO 98/35248 (43) International Publication Date: 13 August 1998 (13.08.98)
(21) International Application Number: PCT/US98/02974 (22) International Filing Date: 11 February 1998 (11.02.98) (30) Priority Data: 60/037,902 11 February 1997 (11.02.97) US (71) Applicant (for all designated States except US): MASSACHUSETTS INSTITUTE OF TECHNOLOGY [US/US]; 77 Massachusetts Avenue, Cambridge, MA 02139 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): FINK, Yoel [US/US]; Apartment 14D, 60 Wadsworth Street, Cambridge, MA 02142 (US). THOMAS, Edwin, L. [US/US]; 14 Apple Ridge Drive, Natick, MA 01760 (US). (74) Agent: OYER, Timothy, J.; Wolf, Greenfield & Sacks, P.C., 600 Atlantic Avenue, Boston, MA 02210 (US).		(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: POLYMERIC PHOTONIC BAND GAP MATERIALS

(57) Abstract

A polymeric photonic band gap structure can be defined by a block copolymeric species, a mixture of homopolymers, or a combination optionally with appropriate dielectric contrast enhancing additives. The structure includes periodic, phase-separated microdomains alternating in refractive index, the domains sized to provide a photonic band gap in the UV-visible spectrum. Another method of the invention involves creating a defect in a polymeric article including a periodic structure of a plurality occurring separate domains. The defect can be created by inserting into the material a plane of a material different from materials defining the polymeric article. According to another method of the invention, a defect is created in a polymeric article, including a periodic structure of a plurality of periodically occurring separate domains, by altering polymeric material in the article. The polymeric material can be altered by removing polymeric material via radiation, by exposing the material to intersecting beams of radiation, by removing the material via etching or the like. A defect can be created in one embodiment by magnetically guiding a heated object through the article.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

POLYMERIC PHOTONIC BAND GAP MATERIALS**Field of the Invention**

The present invention relates generally to polymeric materials that display periodic
5 ordering, and more particularly to a polymeric article defining an optical band gap material.

Background of the Invention

Photonic band gap materials, that is, materials that can control the propagation of
electromagnetic radiation by creating periodic dielectric structures, have been the subject of
vigorous research in recent years. A photonic band gap material is one that prohibits the
10 propagation of electromagnetic radiation within a specified frequency range (band) in certain
directions. That is, band gap materials prevent light from propagating in certain directions
with specified energies. This phenomenon can be thought of as the complete reflection of
electromagnetic radiation of a particular frequency directed at the material in at least one
direction because of the particular structural arrangement of separate domains of the material,
15 and refractive indices of those domains. The structural arrangement and refractive indices of
separate domains that make up these materials form photonic band gaps that inhibit the
propagation of light centered around a particular frequency. (Joannopoulos, et al., "Photonic
Crystals, Molding the Flow of Light", Princeton University Press, Princeton, New Jersey,
1995). One-dimensional photonic band gap materials include structural and refractive
20 periodicity in one direction, two-dimensional photonic band gap materials include periodicity
in two directions, and three-dimensional photonic band gap materials include periodicity in
three directions.

Ho, et al., "Existence of Photonic Gaps in Periodic Dielectric Structures", *Phys. Rev.
Lett.*, 65, 3152 (1990) correctly predicted that a properly-arranged, three-dimensional photonic
25 band gap material would include a complete band gap, that is, that the material would reflect
light of any polarization incident at any angle at a particular frequency. If one or more defects
are created in such a material, the material can serve a variety of useful purposes. Point
defects could define low loss optical resonance cavities, planar defects could define narrow-
band filters, and pathways within three-dimensional photonic band gap materials could define
30 lossless waveguides capable of guiding light around sharp corners, crucial to the creation of
proposed optical computers. Totally-reflective UV or laser shields, and countless other
commercial applications would benefit from relatively simple and reliable techniques for

- 2 -

forming these materials.

Fan, et al., ("Design of Three-Dimensional Photonic Crystals at Submicron Lengthscales", *Appl. Phys. Lett.*, 65, 11, 09/12/94) describe a class of periodic, three-dimensional dielectric photonic crystal structures amenable to submicron-scale fabrication.

5 Fabrication involves creating a layered structure of materials alternating in dielectric constant, and etching (drilling) holes through the article normal to the layered structure. Specifically, the layered structure is created by depositing a layer of silicon on a substrate, etching grooves into the resulting silicon layer, and filling the grooves with silicon dioxide. Another layer of silicon is deposited on the first layer, grooves offset from those of the first set of grooves are
10 etched, and those grooves filled with silicon dioxide. The process is repeated to create the multi-layered structure, through which the holes are etched. Assuming dielectric constants of 12.096 for silicon and 2.084 for silicon dioxide, (both at wavelength = 1.53 microns), the band gap was computed to extend from wavelength = 1.43 microns to 1.64 microns.

Joannopoulos, et al. (referenced above) provides an overview of photonic band gap
15 materials, and their theoretical treatment. Experimental results are reported, including construction of a two-dimensional crystal lattice that reflects essentially all in-plane light within a specified frequency band. Specifically, construction involved etching a triangular lattice of air columns in a crystal via electron-beam lithography (see Wendt, et al., "Nanofabrication of Photonic Lattice Structures in GaAs/AlGaAs", *J. Vac. Sci. & Tech. B.* 11,
20 2637 (1993)). The columns of air were fabricated having a radius of 122.5 nm, the lattice constant was 295 nm, and the columns were about 600 nm tall.

Chen, et al., "Theoretical Prediction of the Optical Waveguiding Properties of Self-Assembled Block Copolymer Films", *Macromolecules*, 17, (1995) describe a lamellar-forming block copolymeric waveguide, and computer calculations of propagation constants and optical
25 field intensity distributions of selected diblock and triblock copolymeric thin-film waveguides. It is reported that by choosing the chemical composition of each block, the refractive index of each layer can be precisely controlled. Where the refractive index of a guiding layer is greater than the refractive indices of the substrate and superstrate layers, a waveguide can result. Chen, et al. report that the domain size of individual lamellae can be varied from tens of
30 angstroms to thousands of angstroms.

Three-dimensional periodicity in block-copolymeric, self-assembled structures are known. (Thomas, et al., "Phase Morphology in Block Copolymer Systems", *Phil. Trans. R.*

SUBSTITUTE SHEET (RULE 26)

- 3 -

Soc. Lond. A., 348, 149-166). Lamellar, cylindrical, spherical, and ordered bicontinuous double diamond morphologies in block copolymeric systems have been identified (see, for example, Helfand, et al., *Developments in Block Copolymers*. 1; Goodman, I., Ed.; Applied Science Publishers: London, 1982; vol. 1, pp. 99-126; Herman, et al., *Macromolecules*, 20, 2940-2942, (1987). Researchers have been successful in incorporation of metallic species, including clusters, selectively in a first but not a second domain of a two-domain species resulting from thermodynamic phase separation of block copolymeric species Sankaran, et al., "Synthesis of Zinc Sulfide Clusters and Zinc Particles Within Microphase-Separated Domains of Organometallic Block Copolymers", *Chem. Mater.*, 5, 1133-1142 (1993); Sohn, et al., "Processable Optically Transparent Block Copolymer Films Containing Superparamagnetic Iron Oxide Nanoclusters", *Chem. Mater.*, 9, 1, 264-269 (1997). Sankaran, et al. and Sohn, et al. pursued goals of creating monodisperse metal/semiconductor clusters in an organized array for the purpose of growing metal clusters in a controlled fashion for electrical, optical, magnetic, and catalytic applications. These and other techniques have shown some promise with respect to several diverse goals. However, there is a need in the art for inexpensive, simple, photonic band gap materials, and it is an object of the present invention to provide such materials.

Summary of the Invention

The present invention provides a series of systems, polymeric materials, and methods associated with photonic band gap materials. The methods include methods of forming such materials and methods of use of such materials, and can be used in conjunction with any of the systems or polymeric materials of the invention. That is, all of the systems described below can be made using the methods of making materials described, and can be used in the methods of using photonic band gap materials. The methods of manufacture and use of photonic band gap materials described herein can be applied to all of the systems or polymeric materials described herein.

In one aspect, the invention provides a series of systems. One system includes a polymeric article having a periodic structure of a plurality of periodically occurring separate domains. The domains include at least a first and a second domain that each have a characteristic dimension from about 50nm to about 1500nm. The article has a refractive index ratio of at least about 1.1 for a continuous set of wavelengths lying within a range from about 100nm to about 10 microns. That is, the article has a refractive index ratio of at least about 1.1

- 4 -

for at least one wavelength domain or continuous plurality of wavelengths, lying within a range of from about 100nm to about 10 microns.

In another embodiment, a similar system is provided. In this embodiment, the first and the second domains each have a characteristic dimension from about 15nm to about 50nm and a refractive index ratio of at least about 1.2 for a continuous set of wavelengths lying within a range from about 50nm to about 1000nm.

In another embodiment, a similar system is provided that has a characteristic dimension of from about 300nm to about 5000nm and a refractive index ratio of greater than 1.0. The refractive index ratio is for a continuous set of wavelengths lying within a range from about 400nm to about 50 microns.

In another embodiment, a system is provided that includes a structurally periodic polymeric structure including a defect in periodicity. The defect is at least partially transparent to electromagnetic radiation in a wavelength range of from about 100nm to about 50 microns. A portion surrounds the defect which is reflective to the electromagnetic radiation.

In another embodiment, a system is provided that comprises a polymeric article including a three-dimensional periodic variation in refractive index.

In another aspect, the invention provides a series of methods. One method involves exposing a portion of a polymeric article in an ordered state, having a pathlength to electromagnetic radiation within a free space wavelength range of from about 50nm to about 50 microns. The article is allowed to inhibit transmittance of the electromagnetic radiation to an extent greater than the article would inhibit that transmittance in a disordered state, at the frequency through the pathlength.

Another method of the invention involves creating a defect in a polymeric article including a periodic structure of a plurality occurring separate domains. The defect can be created by inserting into the material a plane of a material different from materials defining the polymeric article.

According to another method of the invention, a defect is created in a polymeric article, including a periodic structure of a plurality of periodically occurring separate domains, by altering polymeric material in the article. The polymeric material can be altered by removing polymeric material via radiation, by exposing the material to intersecting beams of radiation, by removing the material via etching or the like. A defect can be created in one embodiment by magnetically guiding a heated object through the article.

SUBSTITUTE SHEET (RULE 26)

- 5 -

The systems or method of the invention can include at least one auxiliary refractive modifier in at least one of the first and the second domains. The refractive index modifier can be particulate material, a dye, a polymeric particulate material, a ceramic, semi-conductor, or other particulate material, or the like, and can provide a refractive index ratio in the article of
5 greater than 1, or at least about 1.1, 1.2, 1.3, 1.4, 1.5, 2.0, or 4.0, in other embodiments.

The systems and methods of the invention can involve a polymeric article that has a one-dimensional structure, a two-dimensional periodic structure, or a three-dimensional periodic structure, and can be formed from polymeric materials that are self-assembled from self-assembly of polymeric materials to form separate domains followed by removal of one
10 domain and replacement with a additive material such as a non-polymeric material. That is, first and second domains can be formed by polymeric self-assembly of the first domain and a polymeric precursor of the second domain, followed by replacement of the precursor by a non-polymeric material.

The systems and methods of the invention can involve a polymeric article that includes
15 a block co-polymer having at least two Blocks A and B that are assembled into the first and second domains, respectively. The polymeric article can also include at least three blocks, A, B and C wherein the blocks A and B are self-assembled into the first and the second domains.

The systems and methods of the invention can include polymeric articles that include at least one defect in periodicity. The defect in periodicity can be a point, line, planer defect, or
20 combination thereof, and the defect can have a width, length and height. Where the polymeric article is at least two-dimensionally periodic, the defect can be provided in at least one of the two dimensions, or in two dimensions. Where the polymeric article is three-dimensionally periodic, the defect can be provided in one, two or three dimensions. The defect can be a series of interconnected points, or a line having a width and a length at least five times the
25 width, and other geometric arrangements. A defect can be a continuous pathway that is non-linear, and can be three-dimensionally non-linear. The defect can be in the order of dielectric domains of the structure and can be a defect in refractive index between at least two adjacent domains of a polymeric article.

In some embodiments, the polymeric article of systems or methods of the invention can
30 include a metallic species, rather than a refractive index-modifying species. The metallic species can be a refractive index-modifying species, or another metallic species residing primarily in one domain, selectively.

RECTIFIED SHEET (RULE 91)
ISA / EP

- 6 -

Systems or methods of the invention can include polymeric articles that are periodic arranged structures of a plurality of separate domains. The structure can inhibit transmittance of electromagnetic radiation at a free-space wavelength range from about 50nm to about 50 microns relative to transmission of electromagnetic radiation at the wavelength through a system comprised of the same materials, but in a disarranged state. These structures can inhibit transmittance at a free-space wavelength range of from about 300nm to about 50 microns in other embodiments. A periodic arranged structure can be provided in accordance with systems or methods of the invention that has a photonic band gap in at least one direction within a free-space wavelength range of from about 50nm to about 50 microns. A periodic arranged structure can have a photonic band gap in at least one direction within a free-space wavelength range of from about 300nm to about 50 microns.

Systems or methods of the invention can include polymeric articles that in a disarranged state, are at least partially transparent to light within a wavelength range of from about 100nm to about 10 microns, or a wavelength range of from about 400nm to about 50 microns.

The invention also provides systems that are block copolymers. One block copolymeric species has at least two blocks A and B. The blocks A and B are incompatible with each other such that the block copolymer species is self-assembleable into a periodic structure of a plurality of at least first and second, separate domains, each defined by association of similar blocks of the copolymer species. The periodic structure into which the block copolymer species is self-assembleable is able to contain at least one auxiliary index of refraction enhancing additives such that the first and second domains have a refractive index ratio of at least 1.1 at a wavelength of from about 100nm to about 10 microns, or other refractive index ratios for a continuous set of wavelengths lying within ranges as described herein. In one embodiment, the molecular weight of the block copolymeric species is at least 80,000 Daltons. In another embodiment, the molecular weight is at least 500,000 Daltons, and in another embodiment, at least 2,000,000 Daltons.

Another method of the invention involves a method for processing a block co-polymer. In one embodiment, a block copolymer is processed to produce a phase-separated polymeric multi-domain structure. The structure includes a periodic variation in refractive index of a dimension on the order of from about 100nm to about 50 microns, to the extent that the article defines a photonic band gap structure. The block co-polymer can be allowed to self-assemble

- 7 -

into the phase-separated polymeric multi-domain structure and this can occur in the presence of an applied, electric, magnetic, or mechanical flow field in certain embodiments. In one preferred embodiment, the phase-separated structure is self-assembled in the presence of an applied electromagnetic field.

5 Systems of the invention can include a metallic coating on metallic particles that reside primarily in one domain selectively.

Other advantages, novel features, and objects of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings, which are schematic and which are not intended to be drawn to
10 scale. In the figures, an identical or nearly identical component that is illustrated in various figures, is represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention.

15 Brief Description of the Drawings

Fig. 1 is a schematic illustration of a polymeric one-dimensional photonic band gap material;

Fig. 2 is a schematic illustration of a polymeric one-dimensional photonic band gap material including auxilliary refractive index modifying and periodicity enlarging species;

20 Fig. 3 is a schematic illustration of a polymeric two-dimensional photonic band gap material;

Fig. 4 is a schematic illustration of a polymeric three-dimensional photonic band gap material; and

25 Fig. 5 is a schematic illustration of another three-dimensional photonic band gap material.

Fig. 6 is a Transmission electron microscope micrograph of a layered photonic band gap polymer system showing the formation of periodic dielectric domains;

Fig. 7 is a Small Angle X-ray trace of a layered periodic high dielectric contrast photonic band gap polymer system;

30 Fig. 8 is a Transmission electron microscope micrograph of a two-dimensional photonic band gap polymer system comprising cylinders on a triangular lattice showing the formation of periodic dielectric domains;

Fig. 9 is a Small Angle X-Ray trace of a layered periodic high dielectric contrast two-dimensional photonic band gap polymer system;

Fig. 10 is a Small Angle X-Ray trace of a layered periodic high dielectric contrast two-dimensional photonic band gap polymer system with global order enhanced by annealing;

Fig. 11 is a calculated dispersion relation for low dielectric-constant cylinders in a high dielectric matrix showing an omnidirectional photonic band gap.

Detailed Description of the Invention

The invention provides a polymeric system arranged as a photonic band gap material that inhibits the propagation of a selected frequency of electromagnetic radiation in at least one direction. The term "polymeric system" or "polymeric article" as used herein includes any system or article constructed at least in part from at least one polymer material. The polymeric systems of the invention are inexpensive, allow large area coverage, are mechanically flexible, and, in certain embodiments, self-assemble. The invention provides one, two, and three-dimensional polymeric articles having periodic dielectric structures resulting in polymeric band gap articles that exhibit a band gap inside a specified frequency range in one dimension, two dimensions, or three dimensions. That is, the polymeric articles of the invention inhibit the propagation of electromagnetic radiation at wavelengths in the material ($\lambda_{\text{freespace}}/n_{\text{effective}}$) on the order of the periodicity length of the material in at least one direction, two directions, and a plurality of directions including omnidirectional. With the addition of one or more defects, the arrangement can be used to cause light to propagate along planes, along lines, through non-linear and non-planar continuous pathways, through spaces, and into points. The periodicity of the polymeric systems of the invention and the size of the domains within the systems can be altered, for example by deforming the polymer. For example, periodicity can be altered by mechanical means, such as drilling holes in a system or cutting a system along a specific plane, thermal means, such as selective melting of portions of a system with hot probes or lasers, chemical means, such as selective etching or chemical modification of portions of a system, through selective manipulation of processing procedures, such as processing under the influence of an external field, roll casting, or additions of impurities into one or portions comprising a system, and via a variety of other means hereinafter described or apparent to one of ordinary skill in the art. The dielectric contrast, as well as the periodicity of the periodic dielectric structure, can be varied. In some embodiments, the structure need not be strictly periodic but may be modulated by a field gradient or other modulating means.

- 9 -

The band gap articles of the invention are not limited to use with visible light, although articles operating in the visible light spectrum are preferred. The photonic band gap articles of the invention that operate in the visible light range can be used for low loss waveguides capable of guiding light through non-linear, non-planar pathways that can include sharp corners, or angles of essentially any degree of acuteness. The articles can be used in connection with optical computers, frequency and angle of incidence dependent highly reflective coatings, microcavities useful as optical resonators, totally-reflective visors, etc. The invention avoids problems inherent in connection with most current photonic band gap articles. Most current research efforts concentrate on semiconducting materials such as Si, GaAs, or InP, and are aimed at the construction of two and three-dimensional band gap structures using a variety of lithographic and etching techniques. Problems associated with these approaches include the limited ability of forming intricate, three-dimensional structures on the scales necessary for use as effective band gaps.

The present invention makes use of polymeric materials. The materials can include, but are not limited to, homopolymers, blends of homopolymer, copolymers including random and block copolymers, blends of copolymers, blends of homopolymers and copolymers, and any such systems combined with additives such as dyes, particles, heavy atoms, metallic coating materials, and the like. The systems of the present invention comprise polymeric materials, or mixtures of polymeric materials, or mixtures of polymeric materials and other, non-polymeric materials, and include two or more distinct domains of different composition and/or physical, chemical, or optical properties.

The term "domain", as used herein, defines a distinct region of the system characterized by a particular effective dielectric constant or particular effective refractive index that differs from that of surrounding or adjacent domains. Domains are not necessarily defined by a particular material. These distinct domains are comprised of species, including one or more polymeric species for at least one domain. Where a domain is defined by a polymeric species it is referred to as a "polymeric block." That is, the domains, where polymeric, are based on distinct polymeric blocks that can be comprised of a variety of components comprising distinct regions of the structure, and in each embodiment of the invention at least one domain is polymeric. The polymeric blocks typically are formed from phase-segregated, polymeric species that are immiscible with polymeric species of adjacent phases (which can define domains) from which they are segregated where the species comprising each separate

- 10 -

phase defines separate polymeric blocks corresponding to each phase. That is, adjacent polymeric blocks that can define adjacent, distinct domains can be defined by immiscible mixtures of homopolymer species or random copolymer species, or chain regions (blocks) of a block copolymer that are comprised of a immiscible monomer sequences, or mixtures of the above with or without other non-polymeric additives, where the species in each separated phase or region formed define a polymeric block. Systems comprising multiple polymeric blocks can be comprised of one or more block copolymers or polymeric mixtures involving various blends of homopolymers and/or random copolymers with block copolymers, for example: a homopolymer or random copolymer comprising a block A with a block copolymer comprising blocks A'+B, where A and A' are miscible and are incompatible with B such that the homopolymer or random copolymer A forms a polymeric block in combination with block A' of the block copolymer and block B' of the block copolymer forms a distinct polymeric block; or a homopolymer or random copolymer comprising a block A, a block copolymer comprising polymeric blocks A'+B, and another homopolymer or random copolymer defining a block B', where A and A' together are miscible and form a polymeric block and B and B' together are miscible and form a polymeric block. It is to be understood that the preceding examples are only exemplary, and that those skilled in the art would readily conceive of additional examples which are within the scope and spirit of the invention. In one preferred embodiment, the present invention makes use of self-assembling polymeric systems, for example block-copolymeric systems and blends of various polymers that can include block-copolymers to form one, two, and three-dimensional structures that can, in certain embodiments, be topologically connected. As used herein, "topologically connected" means continuous, in the sense that a particular domain in a periodic, polymeric structure forms a continuous pathway through the structure. This term is defined to include physical connection, or at least proximity to the extent that a photonic band gap material results.

The refractive indices of separate domains of the structures, and periodicity in structural arrangement, are tailored to meet desired criteria. The periodicity in structural arrangement is met by creating separate domains of size similar to the wavelength (in the material comprising the domain as opposed to in a vacuum (freespace)) of electromagnetic radiation desirably blocked by the band gap structure, preferably domains of size no greater than the wavelength of interest. The wavelength of electromagnetic radiation in a material can be related to the wavelength of the radiation in freespace by the following relationship:

RECTIFIED SHEET (RULE 91)
ISA / EP

- 11 -

$\lambda_{\text{material}} = \lambda_{\text{freespace}} / n_{\text{material}}$ where n_{material} is the effective index of refraction of the material at that wavelength. The refractive index ratios between adjacent domains should be high enough to establish a band gap in the material. Band gap can be discussed with reference to two related ratios, the dielectric constant ratio ($\epsilon_1/\epsilon_2 = n_1^2/n_2^2$) and refractive index ratio (n_1/n_2), where n_1 is the effective index of refraction of a first domain and n_2 is the effective index of refraction of a second domain. In general, the larger the refractive index ratio (refractive contrast) the larger the band gap and, in the present invention, band gap is tailored to be above a predetermined threshold and extends in one dimension for one-dimensional systems, two dimensions for two-dimensional systems, and three dimensions for three-dimensional systems.

Preferably, adjacent, dissimilar domains differ in refractive index such that the ratio of the refractive index of one to the other is at least about 1.1 for a continuous set of wavelengths lying within a wavelength range of from about 100nm to about 10 μ m, or, for some embodiments, more preferably at least about 1.2, 1.3, 1.4, 1.5, 2, 4, or 7 within a wavelength range of from about 100nm to about 10 μ m. According to another set of embodiments, these preferred refractive index ratios exist for a continuous set of wavelengths lying within a wavelength range of from about 300 to about 700 nm, and according to another set of embodiments, the ratio of refractive index of one to the other is at least 1.0 for a continuous set of wavelengths lying within a wavelength range of from about 400 nm to 50 μ m, and according to yet another set of embodiments, the ratio of refractive index of one to the other is at least 1.2 for a continuous set of wavelengths lying within a wavelength range of from about 50 nm to 1000 nm. These dielectric structures, exhibiting a band gap in their dispersion relation, cannot support electromagnetic waves at certain frequencies thus those waves are inhibited from propagating through the material.

The polymeric structure should be made of material that, in a disarranged state (not arranged with the periodic structure necessary for photonic band gap properties) is at least partially transparent to the electromagnetic radiation of interest. When the material is at least partially transparent to the electromagnetic radiation of interest, defects in the ordered domain structure of the photonic band gap material define pathways through which the electromagnetic radiation can pass since the criteria for blocking the radiation is destroyed.

Figs. 1-5 are schematic illustrations that are representative of self-assembled, periodic polymeric structures arranged as photonic band gap articles. The propagation of electromagnetic radiation in the articles of the invention represented by Figs. 1-5 is governed

- 12 -

by Maxwell equations, and reference can be made to Joannopoulos (above) for a detailed treatment of the physics involved. In the following discussion of length scales and periodicity, for the sake of simplicity, reference will be made primarily to band gap structures comprised of two separate domains (A and B) with simple one dimensional periodicity. It is to be understood, however, that the invention encompasses systems with greater than two separate domains, and with two- or three- dimensional periodicity. In such systems, as would be understood by those of ordinary skill in the art, the determination of effective domain and periodicity length scales becomes more complex and is affected by factors such as geometric configuration, relative refractive contrast, and others. Incorporated herein by reference Joannopolous, et al. "Photonic Crystals, Molding the Flow of Light", Princeton university press, Princeton, New Jersey, 1995 describes such systems.

Referring now to Fig. 1, a one-dimensionally periodic polymeric photonic band gap article 10 is illustrated schematically. Article 10 is made of a series of essentially planar layers 12, 14, 16, and 18 stacked in the X-Y plane, layers 12 and 16 comprising domains and being defined by a first polymeric species 20 and layers 14 and 18 being defined by a second polymeric species 22. At least one of these polymeric species can also include one or more auxiliary components such as domain dimension modifiers, processing aids, and/or refractive index-modifying species. Polymeric species 20 and 22, including any additive species, preferably differ in refractive index such that the refractive index ratio of the two polymeric species, including any additive species, is as defined above. Thus, article 10 includes a periodic structure of alternating first domains 12 and 16 and second domains 14 and 18 that are dissimilar, and differ in refractive index. Each of layers 12 and 16 has a domain characteristic dimension l_A and each of layers 14 and 18 has a domain characteristic dimension l_B , where the domain characteristic dimensions are proportional to the end to end root mean square (RMS) length of the polymeric species, or copolymer block, comprising each layer in the phase separated state, such that the periodicity, or periodic length, L of the periodic dielectric structure can be represented, for this simple one-dimensional case, as $L = l_A + l_B$, and is on the order of the wavelength (in the material) of electromagnetic radiation 26 desirably blocked by the article. For more complicated configurations, the periodic length L is proportional, but not necessarily equal to the sum of the characteristic domain dimensions. When these criteria are met, exposure of the article, in a direction normal to the planes of the layers 12-18 in the Z axis, to electromagnetic radiation of a wavelength on the order of L ,

SUBSTITUTE SHEET (RULE 26)

- 13 -

results in total reflection of the radiation. Fig. 2 shows an embodiment of a one-dimensional structure having polymeric blocks 20 and 22 which include blocks A and blocks B, respectively, of a diblock copolymer. Polymeric block 22 of the embodiment shown in Fig. 2 is comprised of a mixture of block B of the copolymer, particles 23, and a homopolymer C 24.

5 If polymeric species 20 and 22 are at least partially transparent to electromagnetic radiation 26 to which the article is exposed, and if a defect in periodicity exists in the article that disrupts the ordered, structured arrangement of the article in at least a portion, then the radiation can propagate into and/or through that defect. In one-dimensional periodic systems, a defect can be a change in the index of refraction or the thickness (l) of one layer. An
10 observer located within a defect and looking in the direction of the periodicity will see highly reflective walls, the defect thus being useful in selective propagation of light in photonic band gap materials. A defect can be a continuous pathway, that is, a pathway having a width and a length at least ten times its width. The defect can be a void (i.e., air or other material surrounding the article), one of the polymer species 20 or 22, or any other medium at least
15 partially transparent to the electromagnetic radiation blocked by the defect-free arrangement. Electromagnetic radiation striking the article at regions other than the defect does not propagate through the article, but radiation striking the defect passes through the article to the extent that the defect exists. The radiation of interest, in the defect, can only propagate within the defect due to essentially complete destructive interference in the article beyond the
20 boundary of the defect. Point-like defects (hereinafter referred to as point defects), that is, defects that are small isolated regions, can be created as well, thus forming single, or multi mode cavities.

In a photonic band gap system, such as the one-dimensional photonic band gap material illustrated in Fig. 1, the separate domains 12, 14, 16, and 18 need not alternate in
25 refractive index, but the article can be made up of polymeric species, including any additive species, in sections 12, 14, 16, and 18 that incrementally increase or decrease in refractive index. For example, section 12 can have a refractive index of 1.1, section 14 a refractive index of 1.2, section 16 a refractive index of 1.3, etc., and the article will include a refractive contrast between domains that can be useful.

30 Referring now to Fig. 3, one possible configuration of a two-dimensionally periodic polymeric photonic band gap article 28 is illustrated. Article 28 includes periodicity in both the X direction and Z direction, but not in the Y direction. The article is made up of a plurality

SUBSTITUTE SHEET (RULE 26)

- 14 -

of pillars, or columns, arranged axially in the Y axis, article 28 is defined by a plurality of cylindrical polymeric domains of polymeric species 22 extending in the Y axis of the structure, separated by polymeric species 20. The article is a two-dimensional band gap structure and will reflect radiation of wavelength (in the material) on the order of the characteristic domain dimension of polymeric domain 22 in cross-section (X-Y plane), or the periodic length, which is proportional to the distance between adjacent columns. This radiation will be essentially reflected if directed at the article anywhere in the X-Z plane. The article will pass this radiation in the Y direction. A defect passing through the article in any direction in the X-Y plane, including a defect pathway including sharp corners, will propagate light and serve as a light guide. One way of creating a defect is to remove a series of columns of polymeric species 22 in a pathway.

Referring to Fig. 4, a three-dimensionally periodic polymeric photonic band gap article 32 is illustrated which is periodic in terms of polymeric species 20 and 22 in each of the X, Y, and Z directions at a periodic length L. The structure of Fig. 4 is a double gyroid arrangement of polymeric species 22 surrounded by polymeric species 20. Because periodicity in dielectric constant exists in every dimension, article 32 may be reflective to electromagnetic radiation of a wavelength on the order of L in all directions. A defect, which can be three-dimensionally non-linear (can change in direction of displacement in any direction), will pass electromagnetic radiation of wavelength on the order of L even if the defect includes sharp corners including very acute angles. Since radiation can exist anywhere within the defects and is evanescent beyond the defect boundary, light path bending at any angle including a complete reversal in direction of propagation is possible.

Fig. 5 illustrates a polymeric, three-dimensional photonic band gap article 40 including an arrangement of polymeric species 22, in double diamond configuration, surrounded by polymeric species 20.

Polymeric species 20 and 22 can be arranged periodically, as illustrated in Figs. 1-5, in a variety of ways. According to one technique, polymeric species 20 and 22 define different blocks of a block copolymer. The block copolymer includes blocks of species 20 alternating with blocks of species 22, the copolymer self-assembles into a periodically ordered, structured array. Either of the species (association of blocks) 20 and 22 can also include one or more compatible auxiliary (additive) species. Auxiliary species may be desirable to control characteristic domain dimensions, refractive indices, or both. In other embodiments, a

- 15 -

copolymer can be used that includes more than two phase separable blocks, for example a triblock copolymer.

The polymeric species used for both domains 20 and 22, are preferably below their melt temperature and preferably below their glass transition temperature at service

5 temperatures (i.e., within a temperature range of at least from about -100°C to about 250°C.

For embodiments involving self-assembled polymeric articles, the articles are formed by a mixture of polymeric species, or block copolymer chains each including at least one first polymeric block of species 20 and at least one second polymeric block of species 22

immiscible with the first block. The polymeric species are selected such that, at a temperature
10 above melt temperature or in solution in a suitable solvent, they are segmentally mixed and upon, for example, solidification from a melt or evaporation of a solvent from a solution, the ordered structure is formed including a continuous matrix of amorphous domains. For

embodiments involving block copolymers, the amorphous domains are typically defined by association of the first blocks and second blocks of the copolymer, respectively. In some

15 embodiments, a liquid crystalline domain is incorporated that has anisotropic optical properties (indicatrix; second rank refractive index tensor).

For embodiments where the systems are self-assembled, components for forming a polymeric mixture or block copolymer defining species 20 and 22 as exemplified can be selected according to the following criteria: The polymeric mixture or block copolymer forms
20 separate domains upon phase separation occurring from solidification (including via evaporation from a solvent); one or both components can be below T_g or T_m. Species used in the polymeric mixture or defining the block copolymer form the ordered structure in a manner such that global dimensional stability of the structure exists. As used herein, "microphase separation" means a process in which polymeric blocks are locally segregated to form ordered
25 domains.

That is, a polymeric mixture or block copolymer that defines both species 20 and 22, according to embodiments involving self-assembled articles, is an association of polymer or block copolymer chains in which inter-chain/block, non-covalent chemical attraction such as polar/polar or polar/induced polar interactions, including hydrogen bonding, or
30 nonpolar/nonpolar interactions including Van der Waals interactions, create association between the chains that promotes domain formation while maintaining a degree of dimensional stability required for a particular application. This non-covalent, chemical

- 16 -

attraction of species comprising polymeric blocks to each other results in unique thermodynamic and rheological behavior. At high temperatures, or in solution, the polymeric mixtures or block copolymers form isotropic phases in which the different species comprising the different polymeric blocks are randomly or, in the case of block copolymers, segmentally mixed. Upon lowering the temperature or evaporating away the solvent, or upon precipitation from solution, the repulsion between unlike species or segments increases, causing the polymeric mixture or copolymer to phase separate locally into distinct regions (For the case of block copolymers, each region is composed of one of the block components). These segregated regions subsequently organize into ordered periodic structures, the morphology of which is governed by, among other things, the relative volume fractions of the different polymeric blocks, which can depend on the molecular weight of the species comprising the polymeric blocks and presence of additives. Global dimensional stability is imparted to the material.

The following discussion on miscibility will aid those of ordinary skill in the art in selecting suitable first and second blocks for a copolymer that defines species 20 and 22, or for separate polymers that define these species, or a combination (i.e. a block copolymer that includes one or more auxiliary polymeric species associated with one or more domains). This discussion can be generalized also to a higher order block copolymer, such as a triblock (A-B-C) copolymer. For an example of a diblock copolymer of N total segments, with a 50:50 volume composition, $\chi N > 10.5$ for block segregation. The critical value of χN is larger if the volume composition is different from 50:50. For asymmetric A-B diblock copolymer compositions, the value of χ required for block segregation can be calculated from a well-known formula by L. Leibler (Macromolecules 13, 1602 (1980)), while for A-B-A triblock copolymers, a similar formula by A. M. Mayes and M. Olvera de la Cruz (J. Chem. Phys. 91, 7228 (1989)) can be employed to calculate values of χ required for phase separation for any composition and molecular weight. Those of ordinary skill in the art can carry out this determination technique, and can determine the critical composition for a given diblock or triblock copolymer of any N and composition and can also use similar criteria, readily available, for other types of phase-separable polymeric mixtures.

The molecular weight of polymer or copolymer components defining species 20 and 22 should be selected to be high enough so that a segregated morphology in the service temperature range of the photonic band gap material is maintained. Specifically, the molecular

SUBSTITUTE SHEET (RULE 26)

- 17 -

weight typically is at least about 10,000, preferably at least about 15,000, more preferably at least about 25,000. In one set of embodiments the periodic length L , proportional to the sum of the characteristic domain dimensions l_A and l_B is related to the molecular weight of the species comprising each domain. In this set of embodiments, the molecular weight of polymer or copolymer components defining species 20 and 22 should be at least about 50,000 Daltons, more preferably at least about 100,000, more preferably still at least about 300,000, more preferably still at least about 600,000, and more preferably still at least about 2,000,000 Daltons.

A non-limiting list of polymeric or block copolymeric species can include those that are defined by or contain blocks of polystyrene, polybutadiene, polyisoprene, polycaprolactone, polyethyleneoxide, poly 2-vinyl pyridene, polydimethyl siloxane, and the like. A vast array of different block copolymers, combinations of different homopolymeric species, or combinations of block copolymeric and homopolymeric species can be used in accordance with the invention so long as other criteria described herein are met. Polymers and block copolymers can include a wide variety of side chains that exist naturally, and/or that exist to alter refractive index, segregated polymer domain size, or a combination. For embodiments where structures are self-assembled, each of the first and second polymeric blocks can be a mixture of components so long as the polymer phases separate into the ordered structure described.

Synthetic procedures such as anionic synthesis, Ziegler-Natta polymerization and ring-opening metathesis polymerization (ROMP) (see, for example, Odian, G. "Principles of Polymerization" 2d Ed., Wiley, New York; "Principles and Applications of Organotransition Metal Chemistry", Collman, J.P., Hegedus, L.S., Norton, J.R., and Finke, R.G., University Science Books, Mill Valley, California, 1987, p 590; Grubbs, R.H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F.G.A.; Abel, E.W., Eds.; Pergamon: New York, 1982; Vol. 8, Chapter 54, p 502; Dragutan, V.; Balaban, A.T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerization of Cycloolefins*; Wiley, New York, 1986; Dolgoplosk, B.A.; Korshak, Yu.V. *Russian Chem. Rev.*, 1984, 53, 36) are well-suited for the preparation of a block copolymeric species defining species 20 and 22 with well-defined molecular weights and compositions. Alternatively, block copolymers can be prepared by the reaction of end-functionalized homopolymers, by addition polymerization of one block component onto an end-functionalized homopolymer, or by sequential addition of two

SUBSTITUTE SHEET (RULE 26)

- 18 -

monomer species in a living free radical polymerization. In some embodiments, a photonic band gap article can be prepared by processing, such as melt pressing, or solvent casting techniques such as spin coating or slow evaporation. Technologies for synthesizing and processing such polymeric species are well-known to those of ordinary skill in the art, and includes roll casting or shear casting to achieve near single crystal texture (see, for example, 5 Albalak, R. J., Thomas, E. L., "Microphase Separation of Block Copolymer Solutions in a Flow Field", *J. Polym. Sci., Polym. Phys. Ed.*, p 37-46).

Adjustment of the refractive indices of polymeric species comprising domains 20 and 22 can be made by using, or synthesizing, a polymeric mixture or a block copolymer that 10 includes species 20 and 22 of differing refractive indices; provision of a polymeric mixture or a block copolymer with different species 20 and 22 that phase separate but that do not necessarily include a requisite difference in refractive index and addition of a refractive index-adjusting additives such as an auxiliary polymer that is compatible with one of the phases only (to adjust that phase in refractive index relative to the other phase); provision of a polymeric 15 mixture or a block copolymer with different species 20 and 22 and chemical modification of one or both of the species 20 or 22 to change dielectric constant of one or both; or the like.

Most polymeric species have a refractive index ratio of from between about 1.4 to about 1.7. Accordingly, in some instances a particular combination of polymeric species, or combination of blocks of a block copolymeric species may not have a refractive index contrast 20 needed for establishment of a suitable band gap. For example, polystyrene and polybutadiene have a small difference in refractive index. Therefore, in a polystyrene/polybutadiene mixture or block copolymer it may be desirable to alter the refractive index of one or both of the species.

One technique for selectively altering the refractive index of one domain of a multi- 25 domain polymeric article is to create a polymeric article including a periodic structure of a plurality of alternating separate domains, and changing the refractive index of one domain. Where a block copolymeric species is involved, this will involve changing the refractive index of one of the blocks that has phase-separated into a separate domain. One technique for changing the refractive index of a domain can involve creating a polymeric domain that 30 includes a metal atom on a side group, and forming clusters within that polymeric domain. Formation of clusters containing metal atoms on a polymeric chain can be carried out by forming a microphase-separated structure and diffusing a reactant selectively into the

SUBSTITUTE SHEET (RULE 26)

- 19 -

polymeric domain in which it is desired to create clusters. Such a technique is described by Sankaran, et al., "Synthesis of Zinc Sulfide Clusters and Zinc Particles Within Microphase-Separated Domains of Organometallic Block Copolymers", *Chem. Mater.*, 5, 1133 (1993), incorporated herein by reference. In the technique described by Sankaran, et al., block copolymers of methyltetracyclododecene (MTD) and 2,3-trans-bis((tert-butylamido)methyl)norborn-5-ene(ZnPh)₂ [bTAN](ZnPh)₂ were prepared via ROMP to create block copolymers exhibiting either lamellar or spherical microphase-separated morphology. The zinc atoms in the organometallic domains of the block copolymers were converted to either metallic clusters of zinc or semi-conductor clusters of zinc sulfide by appropriate thermal or chemical treatment. Thermal treatment can involve heating in a bomb reactor and chemical treatment makes use of the fact that the organometallic phase of the microphase-separated structure is compatible with water, and involves treatment of the polymeric species with aqueous H₂S to create ZnS in that domain. Another technique that can be used in the present invention is one similar to that described by Sohn, et al., "Processable Optically Transparent Block Copolymer Films Containing Superparamagnetic Iron Oxide Nanoclusters", *Chem. Mater.*, 9, 264-269 (1997), incorporated herein by reference. Iron oxide nanoclusters are formed, selectively, within one domain of a multi-domain phase-separated polymeric article. In the technique described, the block copolymer [NORCOOH]₃₀[MTD]₃₀₀ (NORCOOH = 2-norbornene-5,6-dicarboxylic acid; MTD = methyltetracyclododecene) is synthesized using an alkylidene initiator (Mo(ChCMe₃Ph)(NAr)(O-*i*-Bu)₂ (Ar=2,6-diisopropylphenyl). The microphase-separated polymeric structure includes topologically-connected carboxylic acid-containing domains that provide a selective diffusion path for aqueous reagents. Accordingly, aqueous NaOH treatment of the assembled structure results in oxidation of iron hydroxide units to iron oxide units in the presence of ambient oxygen. Agitation of the polymeric structure can assist oxidation and flushing and agitation can be used to remove NaOH and NaCl residues. Oxide nanoclusters are formed predominantly within the interconnected domains that originally are NORCOOH. The present invention makes use of this technique for adjusting the refractive index of a polymeric domain, selectively.

In another, similar, technique, a polymeric mixture or block copolymer, does not include species with a metal atom-containing group or a moiety that is reactive with the metal atom-containing group, but includes a polymeric block that is selectively compatible with a homopolymeric species that does include a metal atom-containing group or a moiety reactive

SUBSTITUTE SHEET (RULE 26)

- 20 -

with a metal atom-containing group. Admixture of the polymeric mixture or block copolymer and the homopolymeric species results in a phase-separated structure including one set of domains carrying, selectively, the homopolymeric species. Reaction of the homopolymeric species to form nanoclusters of metal, metal oxide, metal sulfide, ceramics, semiconductors, or the like is carried out as described above to create clusters that reside, selectively or predominantly, in one domain, creating the requisite refractive index ratio. It is not requisite that nanoclusters, or clusters of any type be created according to this refractive index-adjustment technique, only that a particular domain be amenable to receiving, selectively or predominantly relative to others, a refractive index-adjusting species.

Zimmermann, et al., "High Refractive Index Films of Polymer Nanocomposites", *J. Mater. Res.*, 8, 7, 1742 (1993) describe increasing the refractive index of gelatin from 1.5 to 2.5 by creating colloidal PbS within the gelatin via agitation of a gelatin/lead acetate solution while adding hydrogen sulfide. This technique can be applicable to refractive index adjustment of domains of polymeric articles of the present invention.

In another technique, polymeric species including nanoclusters or colloidal particles of refractive index-adjusting species can be created, and later assembled into microphase-separated polymeric domains.

Another technique for adjusting the refractive index of one domain of a multi-domain polymeric article selectively is to form additives such as latex particles, and add these particles to a mixture of polymeric species (including, by definition, different blocks of a block copolymeric species) in which one of the species is compatible with the particles to an extent greater than the other polymeric species (or other block or blocks of a copolymeric species). The additive can be any refractive index-adjusting species such as metal or metal-containing nanoclusters, as described above. The compatibility of the additive for one polymeric species (or block) selectively is great enough that, when a periodic structure of alternating first and second separate domains defined by the different polymeric species is created, the additive will segregate predominantly or selectively in one species to create the requisite refractive index contrast. The additive can be added to the species prior to formation of the periodic structure or, where the additive takes the form of small enough particles, it can be diffused selectively into one or more domains in a carrier that is selectively compatible with those domains. Alternatively, it can be diffused into all domains via one or more carriers, and subsequently removed from one or more domains selectively via a flushing carrier that is compatible

- 21 -

selectively with the domains from which the species is removed, or via a flushing carrier that is compatible with all domains where the additive is selectively incompatible with domains from which it is to be removed. In this arrangement, the additive particulate species may form a high volume percent of one type of domain in a microphase-separated structure. That is, one domain may include the particulate species at a high level, even greater than 50% by volume, and the polymeric species in that domain can define essentially a surfactant that holds the particulate species in place, and together with the particle size, determine the periodicity. This type of arrangement, in which a high-level of additive is held predominantly in one domain by a polymeric species that acts essentially as an additive, falls within the definition of a separate domain in a periodic polymeric photonic band gap structure.

In another technique for adjusting refractive index, a multi-domain structure is formed, defined by different polymeric species or different blocks of a copolymeric species, or both, a monomeric or cross-linkable species is added to the structure that migrates selectively to one domain, and that monomeric or cross-linkable species is polymerized or cross-linked in situ to form a portion of that domain. Species can be graft-polymerized onto existing polymeric species in this manner. In this technique separate monomeric or cross-linkable species can be introduced into separate domains and polymerized, cross-linked, or grafted simultaneously or sequentially to change the refractive index of more than one domain.

In another technique for adjusting refractive index of a domain, selectively, a periodic, polymeric, microphase-separated structure can be fabricated such that one domain is etchable and another is not. That is, the structure is fabricated such that exposure of the structure to an etchant will result in dissolution and removal of one phase selectively while another phase remains intact. With reference to Fig. 3, this could involve exposing article 28 to a chemical reactant that selectively removes species 22, leaving species 20 intact. This can be accomplished when species 20 is chemically inert with respect to the etchant, or is converted to a resistant material (for example, a Si-containing block can be converted to SiO_2) and is robust enough to maintain structural integrity upon removal of species 22. Creating a species 20 that is robust enough to withstand the etchant can involve creating physical rigidity in species 20 via, for example, crystallinity, cross-linking, additive of a dopant selectively to species 20 that causes cross-linking, and the like. After species 22 is selectively removed, it can remain as is (defining a periodic void structure filled by surrounding fluid such as air or another fluid that includes a desired refractive index) or a second species can be added to the

SUBSTITUTE SHEET (RULE 26)

- 22 -

resultant voids and retained in situ via solidification. Solidification can involve precipitation, cross-linking, or the like.

Another technique for adjusting the refractive contrast between different polymeric phases 20 and 22 is by selective staining of one of the periodic phases with a dye.

5 Characteristic dimensions of the individual domains that make up the periodic band gap structure can be controlled by adjusting the length of one or more polymeric species (or blocks of a phase-separated block copolymer) that defines the structure, adjusting polymer processing conditions that increase or decrease the stacking, coiling, or other arrangement of polymer chains (or copolymer blocks), addition of homopolymers, etc. Ring-opening
10 metathesis polymerization, reference above, or anionic synthesis (Cohen, et al.; referenced above), are techniques that can find use in the invention for creating polymer domains of desired size since they well-defined synthetic technique that avoids side reactions and that allows control over molecular weight of particular blocks of block copolymers, or molecular weights of polymeric species. High-molecular-weight multi-block copolymeric systems can
15 be synthesized according to the technique by initiating a polymerization reaction and allowing the reaction to take place, with a particular repeating unit, until a desired characteristic chain length, molecular weight, or number of repeating units is achieved, then synthesizing a second block to a desired extent, and terminating the reaction or adding a third block or repeat of the first block, etc. With high-molecular weight systems, in order to achieve segregation into
20 periodic, microphase-separated domains special processing steps may need to be taken. At higher molecular weights, a polymeric species may become more viscous, thus more time may be required for phase separation to occur. With high-molecular-weight systems, phase segregation can be carried out by dissolving the system in a suitable solvent, removing the solvent slowly and, near the order-disorder transition point, greatly decreasing the rate of
25 solvent removal and optionally adding kinetic energy by vibrating the system via an ultrasonic apparatus, imposing oscillatory or steady shear extensional flow, exposing the system to a static or dynamic electric or magnetic field (especially where one polymeric species or block has a higher relative susceptibility to the field such as via incorporation of an auxiliary species) or combinations thereof or the like.

30 The size of separate polymeric domains can be controlled also via processes described above for adjustment of refractive index, such as incorporation of auxiliary particles, auxiliary homopolymeric species, auxiliary monomeric or cross-linkable species that are polymerized,

SUBSTITUTE SHEET (RULE 26)

- 23 -

grafted, and/or cross-linked in situ, and the like.

For purposes of the invention, a polymeric mixture or block copolymeric species having at least two polymeric blocks each comprised of species having a characteristic RMS chain length in a disordered state of from about 10 nm to about 2000 nm is desirable, or a polymeric mixture or block copolymeric species that self-assembles into a periodic structure having separate domains with characteristic dimensions of, in some embodiments from about 50 to about 1500 nm and in other embodiments from about 300 to 5000 nm and in yet other embodiments from about 15 to 50 nm. The periodic length L is the sum of all the lengths of the distinct dielectric domains contained in one period. For a particular embodiment for which a period contains two domains A and B (e.g. see Fig. 1), the periodic length $L = l_A + l_B$, where l_A and l_B are the characteristic dimensions of the A and B domains. In a particular embodiment for which both domains are defined by a pure A/B diblock copolymer with no additives, the periodic length is related to the RMS molecular chain length in the ordered state $L \propto (n_A + n_B)^{2/3} (\bar{x})$ where n_A and n_B are the respective number of monomer units of the separate polymer block copolymer blocks comprising the domains, and \bar{x} is the average length of the monomer repeat unit of the system, where the structure is ordered as a periodic, phase-separated structure. The relationship is $l_A + l_B = (n_A + n_B)^{1/2} (\bar{x})$ when the system is disordered. As previously discussed, for more complex systems, and systems with higher order dimensional periodicity, the relationship between the periodic length and the characteristic domain dimensions is more complex. These relationships can be used to assist selection of species for use in the invention. Typically, molecular weights of these species will be according to the preferred values noted above. In another embodiment, the periodic, phase-separated polymeric article includes separate domains each made up of at least about 1×10^3 monomer units per domain chain component, preferably at least 5×10^3 , and more preferably at least about 1×10^4 monomer units. This can be adjusted, however, to achieve the desired domain size where a particular domain includes repeating units of particularly high molecular weight, or including side groups that are relatively large and that thereby increase the size of the domain disproportionately to the number of repeat units.

A system can include, in addition to the polymeric species, solvent, preferably non-volatile, in an amount useful in swelling one or both domains, e.g. mineral oil in a polybutadiene/styrene copolymer which will swell the polybutadiene domain. This can be used to control the size of one or more domains. The system can also include other polymeric

- 24 -

or non-polymeric additives for modification of domain dimension, dielectric constant/refractive index, or processability. In addition, a suitable non-polymeric additive can also constitute a separate phase/domain within the photonic band gap structure.

A series of screening techniques can be used to select appropriate polymeric species for use in the polymeric, photonic band gap articles of the invention which include screening of constituent materials, process screening, and optical response screening. In a first test, an absorption measurement is carried out for each constituent of the final material, individually or in combinations, which comprise the domain compositions (e.g. a homopolymer corresponding to each polymeric block type, pure crystallite film, or a combination). Also, a disordered arrangement of the polymeric species (block copolymeric species, mixture of homopolymeric species, etc.) is provided (an arrangement not phase-separated into domains with periodicity on the order of the wavelength of applied radiation) and irradiated to determine its degree of transparency. A material of a useable thickness that is sufficiently transparent and is not totally absorbent throughout the wavelength range of interest is potentially useful.

In another test, materials are selected for suitable dielectric constants. This test can entail performing index of refraction measurements, using an ellipsometer, on a thin film of a pure species or mixture defining a domain composition. The index of refraction can be determined using transmission or reflectivity measurements as a function of wavelength and comparing them to a desirable calculated response (Joannopolouus, et al.). The materials should also be screened for the ability to form structures with appropriate characteristic domain dimensions and periodic length scales. For embodiments using block copolymers, this can be done by measuring the molecular weight of the block copolymers using Nuclear Magnetic Resonance (NMR), Low Angle Laser Light Scattering, or Mass Spectrometry.

Planning and simple screening tests can be used to assess the relative compatibility of components including miscibility, phase separation, chemical stability, and processing stability in order to select suitable components for use as polymeric species 20 and 22, whether they be separate species, different blocks of a block copolymeric species, or a combination. A first and second species should be comprised of components that are immiscible at an appropriate molecular weight and composition. The χ parameter, which is extensively tabulated for a wide range of polymers, can be used to predict miscibility. Once a particular set of species is selected, they can be mixed (if not defined by a block copolymer) and screened for suitability

- 25 -

for use in the invention by analysis via differential scanning calorimetry. If two glass transition temperatures are observed, then the two species (or two blocks of a block copolymer) are immiscible, that is, the desired phase separation has taken place. If only one glass transition temperature is observed, then the components are miscible and phase separation has not occurred, or the glass transition temperatures of the differing species or blocks are coincidentally similar. For the latter situation, if one glass transition temperature is observed, another screening test involving small angle scattering measurements can determine whether phase separation has occurred. Melt temperature and the existence of crystallinity are readily determined by thermal analysis techniques such as DSC or DTA.

Another test involves subjecting the polymeric material or block copolymer to heat and determining the resistance to flow. If the material flows easily as a liquid, microphase separation and resulting dimensional stability at the test temperature does not exist.

Processing methods should also be screened for suitability with desired materials. For example, processing temperatures should be below degradation temperatures. Also, the types and magnitude of the physical forces applied during processing should be conducive to successful assembly of photonic band gap systems, and thus should be able to guide one or more assembly/partitioning events, which give rise to dielectric domains and a proper assembly of the domains into the periodic band gap structure. Processing methods should be avoided that lead to the proliferation of undesired imperfections or that induce undesired physical damage to the materials or structure. The formation of a periodic structure possessing suitable characteristic domain dimensions and periodic length and composition can be verified by small angle x-ray measurements (SAXS), transmission electron microscopy (TEM), optical microscopy, atomic force microscopy (AFM). These methods can also be used to inventory imperfections in the structure.

As another screening test, if creation of photonic band gap materials including phase-separated domains with periodicity on the order of the wavelength of the desired electromagnetic radiation is difficult, but fabrication of phase-separated articles including larger domains is simpler, then a band gap material including domains on the order of, for example, the wavelength of microwaves can be fabricated and tested to determine its properties. If a useful band gap material results, then the material can be adjusted for formation of phase-separated domains of characteristic dimension suitable for the radiation of interest. In some embodiments this characteristic dimension is on the order of 50-1500

- 26 -

nanometers. In other embodiments, the characteristic dimension is on the order of 15-50 nm, and in yet other embodiments, the characteristic dimension is on the order of 300 nm to 5000 nm. The ultimate screening test is the determination of the optical response of the assembled periodic structure and its usefulness as a photonic band gap article over the frequency range of interest. This can be done by comparing calculated and measured dispersion relations while taking proper account of the finite dimensions of the system.

Radiation-propagating or radiation-containing defects or single or multimode cavities can be created in the polymeric, photonic band gap articles 10, 28, and 32 of the invention in a variety of ways. In one-dimensional periodic structures a change in refractive index of one lamellae, or a change in the dimensions of one layer, for example by inserting a layer of another material, or use of an ABC multiblock blended with an AC diblock - effectively creating one layer of B in the multiblock AC system, can be carried out. In two-dimensional structures a point defect can be created by removing a cylinder with a laser or adding latex cylinders before or during formation of the structure. With reference to the structure of Fig. 3, a defect can be created by removing, selectively (via irradiation, etching, or the like) a contiguous series of cylinders of polymeric species 22. A line defect can be formed in two-dimensional and three-dimensional structures by magnetically guiding a heated sphere through the material. A line defect also can be created by drilling a hole, for example using an intense laser beam. A point defect in a three-dimensional structure can be made by adding latex spheres where the size and the index of refraction of the sphere can be controlled. Plane defects can be formed by cutting a three-dimensional structure along a specific plane, rotating the two pieces, and rejoining them together. Cutting a along a specific plane, rotating the two pieces, and rejoining them together can also be used to create a composite structure with a higher effective dimensionality than the initial structure. For example the two-dimensional system shown in Fig. 3 can be bisected along one or more X-Z planes, the sections can then be rotated relative to each other by an angle θ (or different angles for different pairs of sections), and rejoined so that the cylinders 22 are no longer continuous across the planes of bisection (i.e. they are misaligned). This new system can now act as a three-dimensional photonic band gap structure. Point or line defects also can be created by manipulation of intersecting beams of radiation, for example laser beams, ion beams, electron beams, or the like, where the intersecting beams alter the structure enough to create a defect but, along regions of each beam other than the intersecting portions, a structure remains unchanged. In another technique, a hot

- 27 -

magnetic particle can be guided through a structure to create a "burned" pathway that defines a defect by using an alternating current electrical field to heat the particle and steering the particle by use of a direct current or magnetic field.

Another technique for forming defects is via manipulation of processing procedures.

5 For example, anisotropy may be induced in certain directions by applying an external field or by roll casting. Where the defects are point defects, for example by incorporation of an impurity into one or both of the polymeric phases, or introduction of an impurity that will be pinned at polymeric phase interfaces, optionally followed by removal of the impurity via etching or the like, a single-mode resonant optical cavity is defined. A three-dimensional,
10 polymeric photonic band gap structure with a point defect can be used to suppress or induce spontaneous emission from excited atoms placed in those defects. This can be used as a photonic bit or data storage item.

As mentioned above, a variety of polymeric species, including combinations of polymeric species, can be used to create the periodic polymeric photonic band gap structure of
15 the invention. Where block copolymers are used, they can be linear block copolymers, "comb" copolymers, star copolymers, radial teleblock copolymers, dendrimers, or a combination. Those of ordinary skill in the art can select suitable polymers or combinations of polymers to create the phase-separated structure of the invention.

The function and advantage of these and other embodiments of the present invention
20 will be more fully understood from the examples below. The following examples are intended to illustrate the benefits of the present invention, but do not exemplify the full scope of the invention.

Example 1: Formation of Polymeric Photonic Band Gap Article

This prophetic example describes how one would fabricate a polymeric photonic band
25 gap article.

A block copolymeric species of methyltetracyclododecene (MTD) and [2,3-trans-bis((tert-butyl-amido)methyl)norborn-5-ene] [ZnPh₂] are synthesized as described in Sankaran, et al., *Chem Mater.*, 5, 1133 (1993), incorporated herein by reference. A ring-opening metathesis polymerization technique is used and the polymer is synthesized using an amount
30 of precursor and for a length of time sufficient to create blocks each of approximately 500,000 Daltons in molecular weight. The reaction takes place in benzene, vacuum distilled from CaH₂ and stored over NaK and filtered through a sintered glass frit prior to use. The reaction is

- 28 -

terminated with pentadiene.

Periodic structures of alternating separate copolymeric domains are created by casting from solution while, near the point of complete removal of benzene, the system is exposed to ultrasonification for approximately 10 hours while the remainder of the solvent is gradually removed. The polymeric structure then is exposed to H₂S vapors in a suitable solvent for a period of 20 hours. Following this reaction, the polymer is exposed to atmosphere and excess H₂S gas is allowed to dissipate for a period of time of 6-10 hours. The sample is further evacuated at 100° C for 12 hours. The result is a phase-separated article including ZnS clusters in the nanometer size range in one domain selectively, the overall structure having a refractive index ratio between domains of approximately 1.5. If the particular requisite refractive index contrast is not achieved, another refractive index-adjusting species, such as an aqueous dye, is added. Characterization of the resulting polymeric structure is carried out as follows. Molecular weight characterization uses gel permeation chromatography and light scattering. X-ray photoelectron spectroscopy is used to characterized the particulate structure, and NMR spectroscopy (including proton NMR) is used to characterize the block copolymer. A three-dimensional periodic structure results.

A linear defect is created in the structure by guiding a heated article through the structure, the heat supplied by an alternating current field, and the particle being guided through the structure by a direct current field.

Example 2: Formation of a One-dimensional Polymeric Photonic Band Gap Article Comprising Alternate Layers of High and Low Index of Refraction

This example demonstrates the self assembly of a structure of periodically occurring first and second separate dielectric domains in the presence of a flow field. The structure in this example exhibited one dimensional periodicity. The dielectric domains were present in a polymeric article constructed from a P2VP/PI/PS triblock copolymer and an auxiliary refractive index modifying species residing primarily in one of the domains. The domain characteristic size was approximately 20nm for the article fabricated according to this example for both the high and low dielectric constant domains, and the refractive index ratio was estimated to be above 1.1. The fabrication procedure used in this example is general and can be used to fabricate a large number of potentially useful one, two and three dimensional periodic structures at different length scales and refractive indices. To demonstrate the flexibility of the procedure we chose to make a layered dielectric structure. The characteristic